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CVI. *The Behaviour of Electrons in Nitrous Oxide.*

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1. *Introduction.*

IN some recent publications † attention has been drawn to a relation which appears to exist between the absorption spectra of different gases and their relating λ and u curves, where λ is the average proportion of their own energy which electrons with a mean velocity u lose on striking molecules.

Of particular interest in this respect are the gases CO_2 and N_2O, both because they are known to have many similar physical properties and because each absorbs certain infra-red radiations very strongly.

These two gases have been studied respectively by Skinker ‡ and by Skinker and White §, using Townsend's methods.

The experiments with N_2O showed that for values of the ratio Z/p (of the electric force Z in volts/cm. to the gas pressure p in mm.) greater than 3·3 negative ions were present in increasingly large numbers, and so an accurate

* Communicated by the Authors.

† V. A. Bailey and W. E. Duncanson, Phil. Mag., July 1930, p. 145. V. A. Bailey, Phil. Mag., May 1932, p. 993.

‡ M. F. Skinker, Phil. Mag., November 1922, p. 994.

§ M. F. Skinker and J. V. White, Phil. Mag., October 1923, p. 630.

knowledge of the Townsendian energy factor k and the drift-velocity W of the electrons could not be obtained.

Accordingly it was decided to apply to N_2O the methods of investigation, developed in Sydney, which have been specially designed to study the motions of electrons in streams which also contain large numbers of negative ions *.

The instrument with variable slit-intervals which had been used for the investigations on NH_3, H_2O, and HCl was used for the majority of the observations on N_2O, but a different procedure was adopted which has certain advantages.

Before describing this it is necessary to give a brief résumé of the general principles on which are based the methods for the determination of values of the Townsendian factor k, the drift-velocity W, and the attachment-coefficient α under conditions where negative ions are present in notable quantities.

The instrument in which streams of negative electricity are studied consists essentially of five parallel disks P, 0, 1, 2, 3 kept at the potentials necessary to maintain a uniform electric force Z throughout, the disks 0, 1, 2 containing parallel and superposed slits each 4 mm. wide and respectively 1·5, 6·2, and 7·2 cm. long. The interval c between the disks 0 and 1 is always the same as that between 1 and 2.

Under the action of the ultra-violet light the plate P emits negative electricity which moves through the gas and ultimately reaches the electrodes 1, 2, and 3 in proportions which, for any particular gas, depend on the values of Z, c, and the pressure p of the gas.

The ratios S_1 and S_2 are measured, where S_1 is the fraction of the total stream, approaching the disk 1, which passes through the slit in the disk, and S_2 is similarly related to disk 2.

The value of the quantity

$$a = S_1\left(\frac{R-S_2}{R-S_1}\right)$$

can thus be determined, where R is the value which S_1 and S_2 would have were the streams composed entirely of negative ions. This value is known in terms of the ratio Z/c, and can be represented as a function $R(Z/c)$ of Z/c by means of a curve.

* V. A. Bailey, Phil. Mag., October 1925, p. 825; April 1930, pp. 560, 625. V. A. Bailey and J. D. McGee, Phil. Mag., December 1928, p. 1073. V. A. Bailey and W. E. Duncanson, Phil. Mag., July 1930, p. 145.

The quantity a can also be expressed as a known function of k and α thus:

$$a = \mathrm{R}(\mathrm{Z}/kc)e^{-\alpha c}, \quad \ldots\ldots (1)$$

and so provides one relation between the two unknown quantities k and α.

A second relation between the two latter can be similarly obtained by determining the value of a corresponding to any other set of values of c, p, Z in which the ratio Z/p is the same as with the first set. By means of these two relations the values of k and α can then be obtained.

To determine the drift-velocity W a uniform magnetic field of intensity H is applied parallel to the electric force Z and is adjusted to a value H_0 at which S_2 becomes equal to R.

The value of W is then obtained by means of the formula

$$\mathrm{W} = \frac{\mathrm{Z}}{\mathrm{H}_0}\sqrt{k-1}, \quad \ldots\ldots (2)$$

since the value of k is known.

In the investigations * of the behaviour of electrons in NH_3, $\mathrm{H}_2\mathrm{O}$, and HCl the necessary two relations between k and α were obtained by determining the quantity a_1 corresponding to a set of values of c, p, and Z and the quantity a_n corresponding to a homologous set nc, np, *and* nZ. This may conveniently be named the Homologous Method.

In the following section a method is described which enables a second relation between k and α to be obtained without changing the values of c, p, and Z.

2. *The Magnetic Method.*

The value of the quantity a in the presence of the magnetic field H is given by the expression

$$a_h = \mathrm{R}(\mathrm{Z}\sigma/kc)e^{-\alpha c}, \quad \ldots\ldots (3)$$

where

$$\sigma = 1+(\mathrm{HW}/\mathrm{Z})^2. \quad \ldots\ldots (4)$$

Combining (3) and (1) and writing

$$y = \log_{10}a_h - \log_{10}a \quad \ldots\ldots (5)$$

leads to the relation

$$y = \log_{10}\mathrm{R}(\mathrm{Z}\sigma/kc) - \log_{10}\mathrm{R}(\mathrm{Z}/kc). \quad \ldots (6)$$

* V. A. Bailey and J. D. McGee, Phil. Mag., December 1928, p. 1073. V. A. Bailey and W. E. Duncanson, Phil. Mag., July 1930, p. 145.

When $H=H_0/2$ then, by (2) and (4)

$$\sigma = \tfrac{1}{4}(k+3),$$

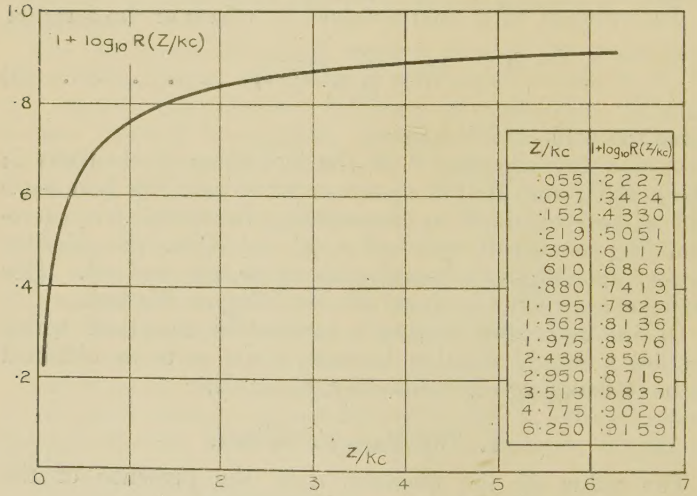
and so

$$y = \log_{10} R\left(Z\left(\frac{k+3}{4kc}\right)\right) - \log_{10} R(Z/kc).$$

For given values of c and Z this relation between k and y can be represented by means of a curve as in fig. 2.

The two curves shown both correspond to $c=4$ and respectively to $Z=16$ and $Z=24$. They were determined with the help of the curve in fig. 1 which has been derived from the values* of R calculated in 1925.

Fig. 1.



Z/Kc	1+log10R(Z/Kc)
·055	·2227
·097	·3424
·152	·4330
·219	·5051
·390	·6117
610	·6866
·880	·7419
1·195	·7825
1·562	·8136
1·975	·8376
2·438	·8561
2·950	·8716
3·513	·8837
4·775	·9020
6·250	·9159

When the values of a and a_h have been determined experimentally with $H=0$ and $H_0/2$ respectively, the value of $y=\log_{10}a_h-\log_{10}a$ is known, and so by means of fig. 2 the value of k can be obtained. This now allows the value of α to be derived from $\log_{10}a$. It is conveniently done with the help of fig. 1, using equation (1) in the form

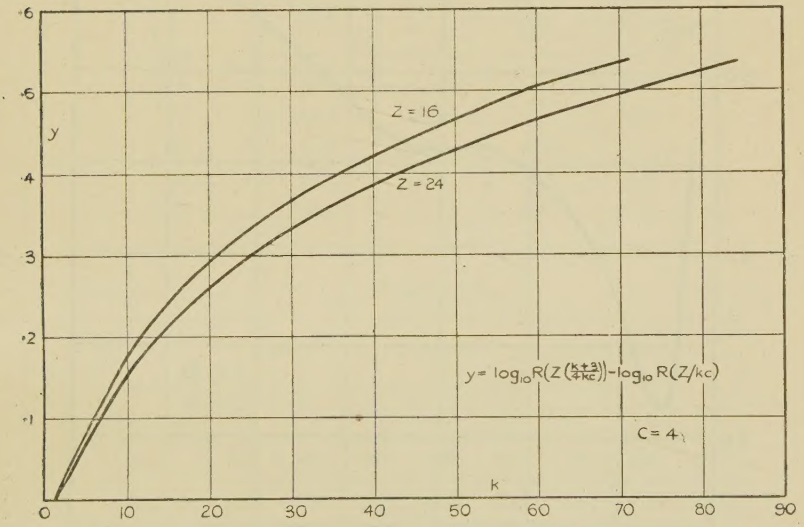
$$\alpha c = 2{\cdot}3\{\log_{10} R(Z/kc) - \log_{10} a\}.$$

The Magnetic Method, as this may be called, offers certain advantages over the Homologous Method, namely :—

* V. A. Bailey, Phil. Mag., October 1925, p. 833.

1. The instrument can be constructed more simply and accurately, since the electrodes are fixed in position.
2. The errors in the magnitude and uniformity of the electric field, due to contact-potentials, are less, since c is never less than 4 cm.
3. The error, due to the neglect of forwards-diffusion in calculating R, is less.
4. At pressures less than 1 mm. of Hg the error due to the mean free path becoming comparable with the slit-widths is less.

Fig. 2.



3. *Preparation of pure* N_2O.

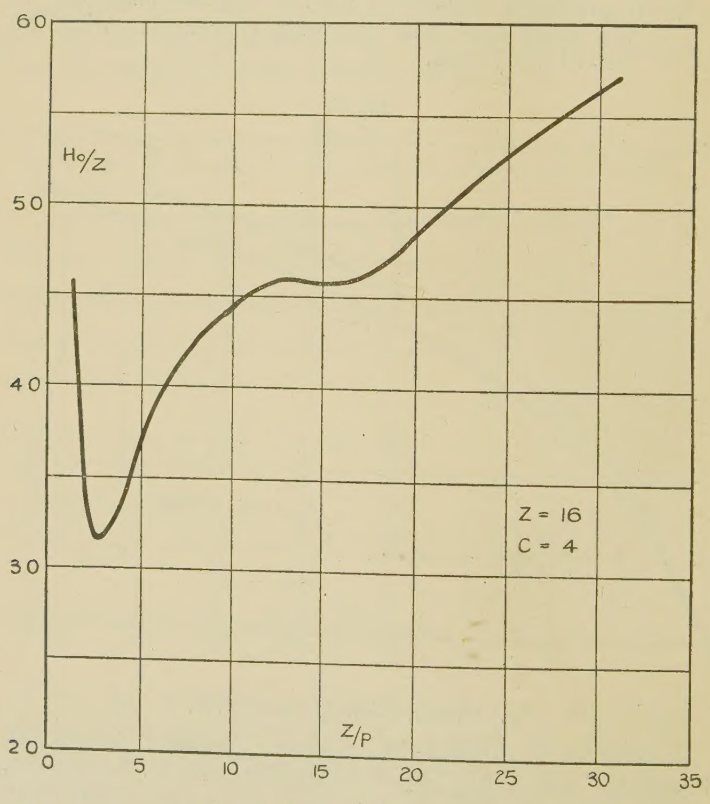
A cylinder of nitrous oxide, labelled "Certified Laboratory Products," was kindly lent to us by Professor C. E. Fawsitt. From this 27 litres of gas were taken and fractionally distilled twice by means of liquid air and a mixture of carbon-dioxide snow, and ether. The purified gas was then stored in glass reservoirs over KOH or P_2O_5.

Most of the observations were made with the middle third of the second distillation which was stored over KOH. Observations were also made with some of the last third in the second distillation which was stored over P_2O_5, and were found to be in good agreement with the others.

4. *The Observations.*

The first systematic observations made were on the values of the ratio H_0/Z for different values of the pressure p when the intensity Z was kept constant, and usually at 16 volts/cm. These are represented by the curve in fig. 3 and, with repetitions, number about seventy.

Fig. 3.



The theory shows that, for a given gas, the ratio H_0/Z depends only on the ratio Z/p. Since this result is applied in the Magnetic Method it was tested by determining the values of H_0/Z corresponding to a given value of Z/p but with different forces and slit-intervals. These are given in Table I., from which, by comparing the numbers in the same row, it will be seen that when Z/p is constant the ratio H_0/Z is also constant, to within about 3 per cent.

In order closely to explore the properties of the gas observations were made in a series of "runs," one example of which is shown in Table II., where p is expressed in mm. of Hg and Z in volts/cm.

The quantities a and a_k were then observed for different values of p with Z kept constant, the values of $H = H_0/2$ used in the determination of a_k being derived from the curve in fig. 3.

Table I.

Z/p.	H_0/Z.			
	Z=16. $c=4$.	Z=8. $c=4$.	Z=12. $c=2$.	Z=8. $c=2$.
4	34·1	...	...	35·4
12	46·1	47·2	...	46·1
16	45·7	48·5	44·6	...
24	52·2	53·6	50·1	...
32	58·1	...	56·1	...

Table II.

	$c=4$.		Z=16.		$S_2=·780$.			
p	8·0	7·0	6·0	5·2	4·6	4·0	3·6	3·2
H_0	527	504	504	508	527	543	568	593
Z/p	2·00	2·30	2·67	3·08	3·48	4·00	4·44	5·00
H_0/Z ...	32·9	31·5	31·5	31·8	32·9	33·9	35·5	37·1

Examples of such observations are given in Table III.

Two series of observations were made, one with Z=24 and the other with Z=16. The curves in fig. 4 represent the values so obtained of $1+\log_{10}a$ and $1+\log_{10}a_k$ in terms of Z/p.

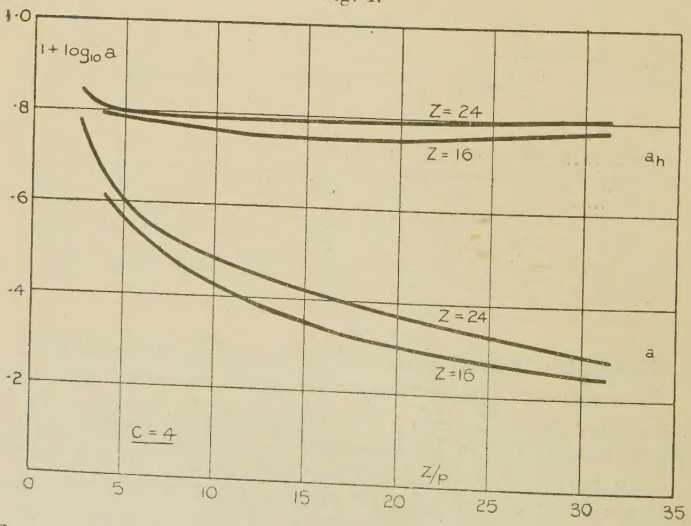
The value of k for a given value of Z/p is obtained as follows from either pair of curves marked with the same value of Z. The difference y of the ordinates corresponding to this value of Z/p is determined, and the abscissa corresponding to this value of y in fig. 2 is the required number.

Examples of such determinations are shown in Table IV., where k_{24} and k_{16} are the values obtained respectively with

TABLE III.

	$c=4$.		Z=24.		R=·820.	
p	6·0	3·0	2·0	1·5	1·0	0·75
S_1	·525	·407	·350	·316	·274	·222
S_2	·559	·490	·434	·405	·371	·324
a	·465	·325	·287	·260	·225	·184
H	400	510	553	546	619	698
S_{1h}	·702	·660	·677	·670	·665	·658
S_{2h}	·707	·675	·687	·683	·672	·662
a_h	·672	·598	·630	·612	·635	·642
Z/p	4	8	12	16	24	32

Fig. 4.



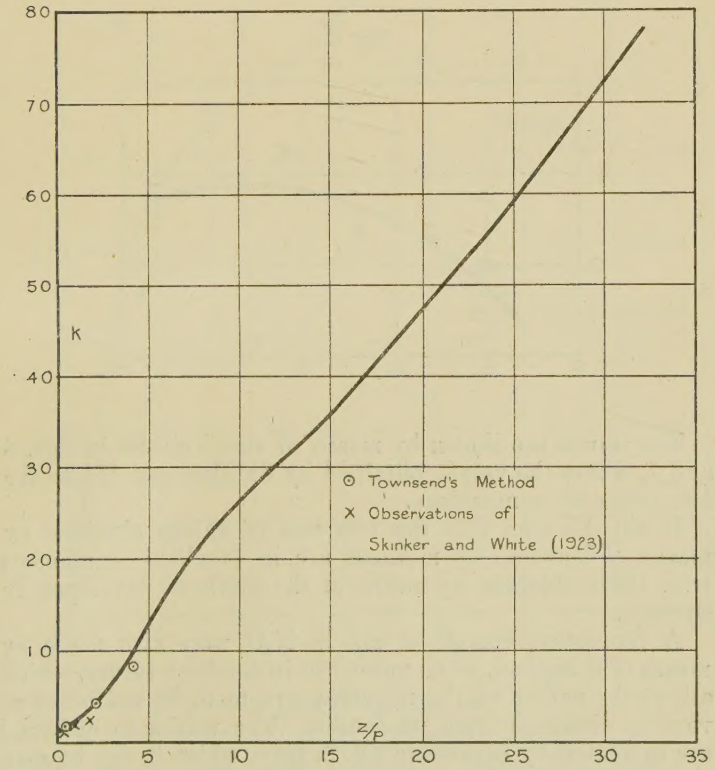
Z=24 and Z=16. The close agreement between the numbers in the last two rows may be regarded as further confirmation of the soundness of the principles adopted.

The curve in fig. 5 represents the values of k in terms of Z/p.

TABLE IV.

Z/p	4	8	12	16	24	32
k_{24}	9·65	21·8	30·7	39·0	58·0	80·0
k_{16}	10·15	21·2	30·3	37·6	56·8	77·0

Fig. 5.



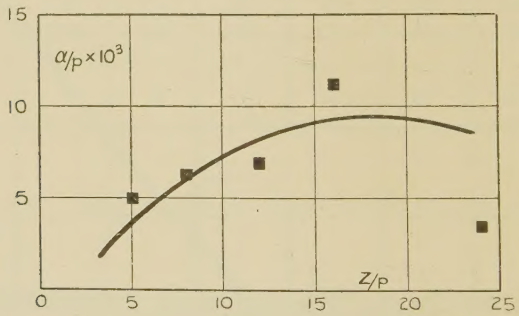
The value of α/p for a given value of Z/p is now obtained as follows. The value of k being known, that of the quantity $1+\log_{10}R(Z/kc)$ is obtained from the curve in

fig. 1, and the value of $1+\log_{10}a$, obtained from fig. 4, subtracted from it; this gives the value of $\alpha c/2{\cdot}3$ and so that of α/p. This quantity, obtained with $Z=24$ and $Z=16$, is represented in terms of Z/p by the curve in fig. 6.

The values of W are derived from the curves in figs. 3 and 5 by means of the formula (2), and are represented in terms of values of Z/p down to 1 by the curve in fig. 7.

In conformity with the results of Skinker and White it was found that when Z/p was less than 2·7 there were very few negative ions present. Accordingly observations of k and W in this region were also made on our sample of N_2O by means of Townsend's methods, in which W is determined by deflecting the stream of electrons with a transverse magnetic field.

Fig. 6.



The results are shown by means of small circles in figs. 5 and 7, where the values obtained by Skinker and White are also given for comparison.

It will be seen that the two sets of values obtained by means of Townsend's methods are in excellent agreement with those obtained by means of the methods developed in Sydney.

A few measurements of α/p in N_2O were also made by means of a method, to be published in the near future, which allows the nature of the negative stream to be examined at various distances from its source. The values so obtained are indicated by squares in fig. 6, from which it will be seen that they confirm the conclusions of the Magnetic Method.

From these determinations of k, W, and α/p the values of the following quantities have been deduced by means of equations (7):—

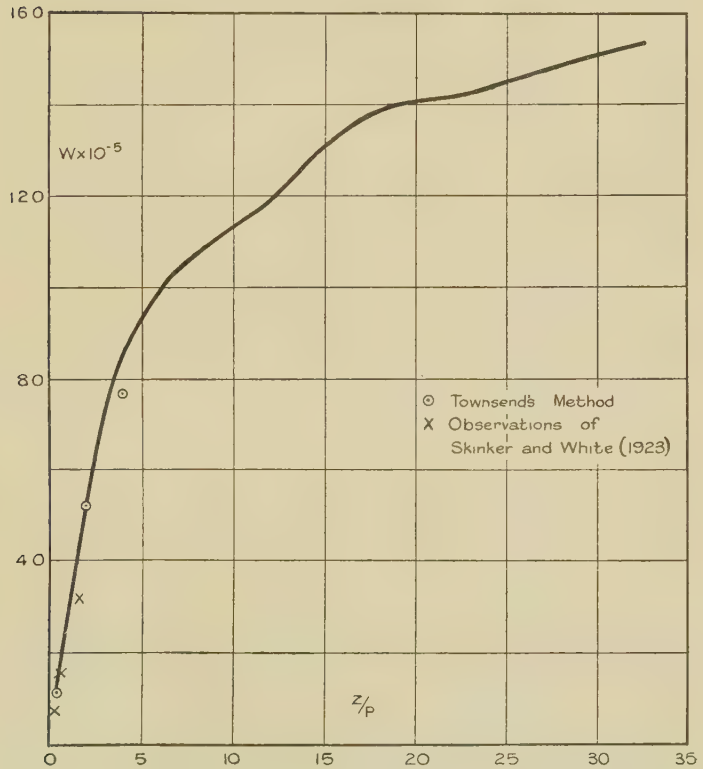
u, the mean velocity of agitation of an electron;

L, its mean free path at 1 mm. pressure;

λ, the mean fraction of its own energy which is lost at a collision with a molecule;

h, the probability of a negative ion being formed at a collision.

Fig. 7.



$$\left.\begin{aligned} u &= 1{\cdot}15\times10^{7}\sqrt{k}\ \text{cm./sec.},\\ \mathrm{L} &= 8\times10^{-9}\mathrm{W}\sqrt{k}/(\mathrm{Z}/p)\ \text{cm.},\\ \lambda &= 1{\cdot}86\times10^{-14}\mathrm{W}^{2}/k,\\ h &= 7\times10^{-16}(\alpha/\mathrm{Z})\mathrm{W}^{2}. \end{aligned}\right\} \quad . \quad . \quad (7)$$

The results of such calculations are given in Table V., and

in respect of L and λ are also represented by the curves in figs. 8 and 9.

For comparison the corresponding curves for CO_2 are also shown. These have been obtained by J. B. Rudd by means of the Magnetic Method, and are not very different from the curves which represent the results obtained by

Table V.

Z/p.	k.	$W\times10^{-5}$. cm./sec	$(a/p)\times10^{3}$.	$u\times10^{-7}$. cm./sec.	$L\times10^{2}$. cm.	$\lambda\times10^{2}$.	$h\times10^{4}$.
1 ...	2·4	25·9		1·78	3·21	5·22	
2 ...	4·1	53·4	·0	2·33	4·32	12·90	·00
2·5...	5·2	64·8		2·62	4·72	15·02	
2·75..	5·75	68·9		2·76	4·82	15·37	
3 ...	6·4	73·1	1·3	2·91	4·93	15·54	·16
3·25..	7·1	76·7		3·06	5·03	15·38	
3·5...	7·8	79·7		3·21	5·10	15·08	
4 ...	9·5	85·5		3·54	5·28	14·34	
5 ...	13·0	93·2	3·7	4·15	5·37	12·40	·45
6 ...	16·4	99·4		4·66	5·37	11·20	
8 ...	21·9	107·6		5·38	5·04	9·81	
10 ...	26·4	113·4	7·3	5·91	4·58	9·08	·65
12 ...	30·6	118·9		6·36	4·38	8·61	
14 ...	34·7	126·5		6·77	4·26	8·56	
16 ...	38·7	133·7	9·3	7·15	4·16	8·60	·73
18 ...	43·0	138·2		7·54	4·03	8·26	
20 ...	47·8	140·5		7·94	3·88	7·64	
22 ...	52·5	141·8		8·34	3·74	7·13	
24 ...	57·5	143·8	8·5	8·72	3·64	6·68	·51
28 ...	68·0	148·2		9·49	3·49	6·01	
32 ..	79·0	152·5		10·22	3·39	5·48	

Skinker * in 1922. The details of this investigation will be published in the near future.

5. *Discussion.*

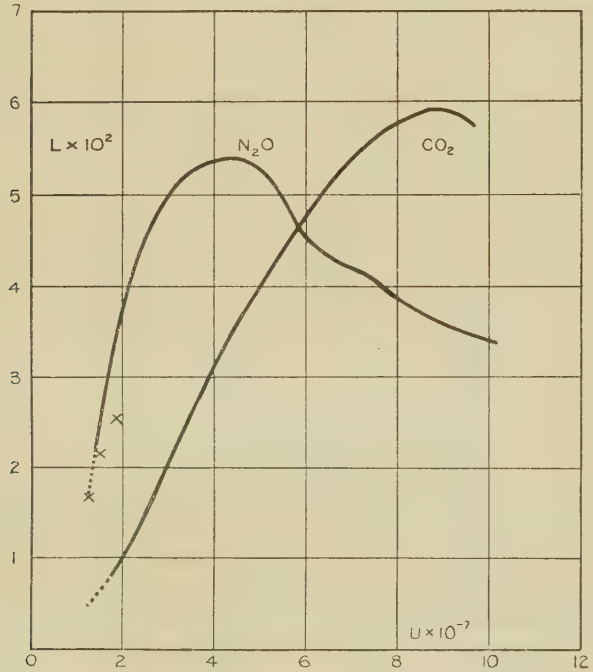
It will be seen from figs. 8 and 9 that the variations of L and λ with the velocity u are roughly similar for the gases N_2O and CO_2; this may, perhaps, have been expected, since

* M.F. Skinker, *loc. cit.*

these gases are similar in regard to many other physical properties.

The λ-curve for N_2O has a remarkable peak corresponding to a velocity of about 3×10^7 cm./sec. At this mean velocity the electron loses on an average about 15·5 per cent. of its own energy at a collision with a molecule of N_2O. This is the largest recorded proportional loss observed for such slow electrons in any gas. It may be mentioned that Brose and Keyston * have stated that they found that the λ-curve of

Fig. 8.



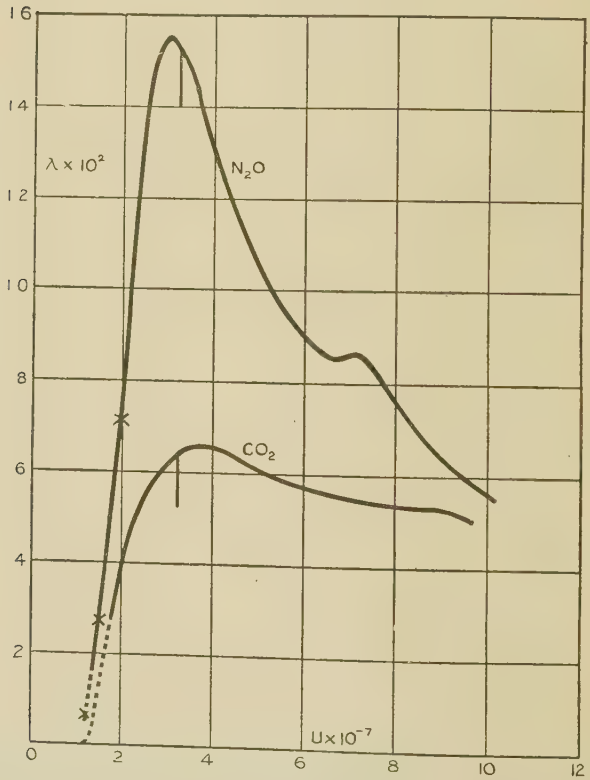
methane lies above the λ-curve of any other gas until then investigated, but as they have not yet published their results in detail a comparison of methane with N_2O is not possible here.

The centres of the strongest infra-red absorption bands in N_2O and CO_2 are represented by short vertical lines whose positions correspond to electronic energies equal to the respective quanta of radiant energy. It will be seen that these lines are close to the peaks of their respective gases.

* H. L. Brose and J. E. Keyston, 'Nature,' November 22, 1930.

The λ-curve for N_2O has a second, but much smaller, peak corresponding to the velocity 7×10^7 cm./sec., *i. e.* corresponding to a wave-length of light of about ·9 μ. There does not appear to be any positive information published about the absorption-spectrum of N_2O near this wave-length; but even if no absorption be observed here there may exist other known ways of associating a molecule of N_2O with the

Fig. 9.



quantity of energy, 32,000 calories per gram-molecule, corresponding to the velocity 7×10^7 cm./sec. Dr. T. Iredale suggests that decomposition of the gas may take place with electronic velocities near this value, as the energy of activation * of N_2O is about 30,000 calories for one gram-molecule. It is hoped to examine this point experimentally.

* Hinshelwood and Burk, Proc. Roy. Soc. A, cvi. p. 284 (1924). Volmer and Kimmerov, *Zeit. f. phys. Chem.* B, ix. p. 141 (1930).

CVII. *Note on Cathode Sputtering.* *By* Prof. F. H. Newman, *D.Sc., A.R.C.S., University College, Exeter* *.

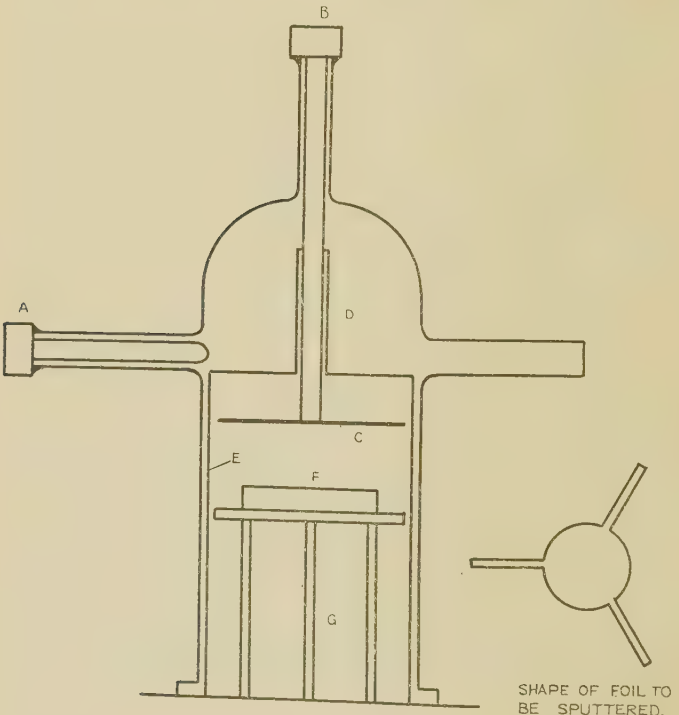
THE rate of cathodic deposition of a metal is increased by sputtering in a heavy gas—being about five times faster in argon than in hydrogen. Some experimenters prefer to sputter with comparatively high pressures in noble gases, and under these conditions high current density can be employed ; the mirrors, being well outside of the dark space, may be sputtered very rapidly without becoming too hot. In less elaborate technique, however, where it is not desired to use noble gases, it is sufficient if the vacuum is maintained as high as possible to permit a discharge. If the gas pressure is not very low a brownish-coloured deposit—due probably to the decomposition of the carbon oxides present in the apparatus—is obtained on the sputtered surface, and even if the metal is deposited the resulting mirror is dark, its reflectivity being poor.

A successful sputtering technique should give a mirror of good reflecting properties, a rugged metal film which adheres to the glass, and good mirrors which are easily produced without failure. In some cases methods for cooling the cathode are advised, but these entail the introduction of a considerable amount of metal into the sputtering chamber. Metals always contain large quantities of occluded gases which are liberated while the electrical discharge is passing, and are detrimental to the formation of good mirrors. Cooling is not necessary. On the contrary it has been found by the author that a more rugged mirror is obtained if the glass to be "mirrored" is first heated before introduction into the chamber. Cartwright † has previously noted the same effect. If high current density is used the sputtering can be done intermittently, and the glass does not become too hot.

Usually the sputtering chamber is made of glass, but fractures often occur, and the author has found that a quartz chamber is more satisfactory in this, and other respects. The figure shows the sputtering chamber employed for "platinizing," "silvering," etc. the mirrors used in interferometers and similar instruments. The chamber should be as large as possible—although the present one is only 450 c.c.,—for then a more even and rapid deposit

* Communicated by the Author.
† Rev. Sci. Inst. i. p. 758 (1930).

of the metal is obtained. To overcome the difficulty of sealing-in the aluminium electrodes A, B, their ends were of slightly greater diameter than that of the outside of the quartz tubes into which they were sealed. These ends form a good fit with the extremities of the tubes, and hard Khotinsky cement, or ordinary sealing-wax, can be placed around the metal–quartz junction. In spite of the wax softening during a prolonged electrical discharge it still acts



Sputtering apparatus.

as a good seal, and there is no danger of the electrodes being drawn into the chamber. The end of the cathode electrode is made to screw on to the rest of the electrode so that the latter may be removed from the chamber when it is desired to change the sputtering metal. The latter, in the form of foil, is cut as shown and the ends of the strips wired to the aluminium rod. A glass tube D is placed over the cathode rod to prevent the electrical discharge from passing directly to the aluminium instead of to the sputtering metal.

The surface to be sputtered, F, must be carefully cleaned and dried, and, after heating, is supported on a simple type of glass table G, so that it is about 4 cm. away from the sputtering metal. To keep the sputtered metal from the walls of the quartz chamber a glass tube E, open at both ends and of slightly smaller diameter than the discharge vessel, is placed inside the latter. At the conclusion of each sputtering process this glass tube can be removed and cleaned, and so the progress of the metal deposition can be followed. In addition, this tube can be more easily cleaned than the internal walls of the sputtering chamber. The latter has a ground flange and fits on a glass base plate. A little Khotinsky cement, or sealing-wax, round the junction of the flange and base plate forms an effective seal. This part of the apparatus never gets hot and the wax does not soften. A Cenco-Hyvac pump, running continuously, completes the equipment ; the high-tension current is obtained from a 4000 volt transformer with a rectifying valve in the circuit. Glass surfaces can be "half-platinized" in half a minute and completely "platinized" in about five minutes. With silver these times are approximately halved.

At first it was found that in some cases the sputtered glass surface became frosted in appearance some time after removal from the sputtering chamber. This trouble was eliminated by a preliminary heating of the glass to 150°–200° C. before it was placed in the chamber. The frosting is not due to the contraction of the film when the glass cools since it only occurred with certain glasses.

The apparatus can also be employed to render quartz fibres conducting by sputtering platinum on them. In this case the cathode is a cylinder of platinum gauze, open at both ends and suspended from the end B. The fibre to be sputtered is supported inside the cylinder.

CVIII. *Absorption Measurements and Transition Probabilities for the* A (0, 0) *and* B (0, 1) *Bands of Oxygen.*

By W. H. J. Childs, *B.Sc., Ph.D., Davy-Faraday Research Laboratory* *.

[Plate XXVIII.]

THE A and B bands of oxygen, belonging to the atmospheric oxygen bands, so-called since they are observed as telluric lines in the solar spectrum, may also

* Communicated by the Author.

be observed under laboratory conditions with quite moderate thicknesses of air. The more intense lines of the A band, for example, are already to be seen with a three-metre concave grating, where the total thickness of the absorbing layer is some six metres, equivalent roughly to about one metre of pure oxygen at atmospheric pressure. Such favourable circumstances have led to these bands being studied in considerable detail during the last few years, with the consequence that their structure is definitely known [1], [2], and the electron transition has been fixed as an intercombination between a $^3\Sigma$ ground level and a metastable $^1\Sigma$ upper level. The distribution of intensity among the lines, which until recently theory [3] did not supply for intercombination bands, has been measured with some accuracy [4], and the results have been applied to a quantitative estimation of the relative proportions in "chemical" oxygen of the three isotopes $O_{(16)}$ $O_{(17)}$ $O_{(18)}$ [5], information of some importance for the comparison of chemically determined atomic weights with those determined by the mass-spectrograph. This is by no means all the information which may be derived from these bands; it is intended in the present paper, firstly by a comparison of the total absorption of the A-band with that of the B-band, to determine the relative probabilities of the vibrational transitions $0 \rightarrow 0$ and $0 \rightarrow 1$, and, secondly, to relate the total absorption with the number of absorbing centres.

Experimental.

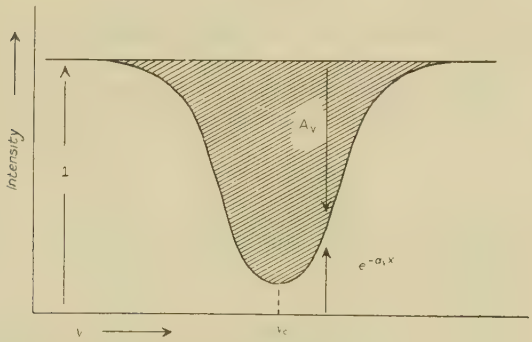
The plates and microphotometer records were obtained during a previous investigation. The experimental details can be found described in *Zeits. f. Phys.* lxviii. p. 362 (1931), to which for brevity the reader is referred. It will suffice here to say that the photographs, reproduced in Pl. XXVIII, were obtained in the first order of a concave grating (focus 6 metres, dispersion 2 A.U. per mm. and resolving power 100,000) on two successive clear sunny evenings in June 1930, under practically identical weather conditions and at but slightly differing times. The mean time (local time) at which the A-band exposure was made was 19 h. 5 m. and that for the B-band 18 h. 53 m., so that, assuming the height of the homogeneous oxygen layer to be 7·22 km. we have corresponding path

lengths of 49·7 km. and 41·4 km. respectively. The plates were then photometered and the microphotometer records carefully enlarged about four times for convenience of measurement. The plate characteristics for each region had been determined beforehand, and from these it was possible to construct transparent scales which, when placed over the records, enabled intensities (in arbitrary units, of course) to be read off directly.

The Method of Measurement.

The A-band, involving the vibrational jump 0→0, and the B-band with a jump from 0→1 have a common initial state, so that a direct comparison of intensities

Fig. 1.



Transmission at $\nu = e^{-\alpha_\nu x}$.

The integrated absorption coefficient $\alpha = \int_0^\infty \alpha_\nu d\nu$.

The total absorption (shaded area) $A = \int_0^\infty A_\nu d\nu$.

$$= \int_0^\infty (1 - e^{-\alpha_\nu x}) d\nu.$$

gives at once the transition probability ratio p_{00}/p_{01} which it is desired to find. But the "intensity" of an absorption line, the quantity having a theoretical significance and which can be described by expressions of the form $J = C.\, i.\, \exp.(-E/kT)$, is measured by the integrated absorption coefficient $\alpha = \int \alpha_\nu \, d\nu$ (fig. 1).

From the experimental point of view this is a quantity not at all easy to determine directly, for it requires that the recording instrument shall reproduce exactly the line contour, a requirement which no instrument of finite resolving power can fulfil. There is, fortunately, in the case of oxygen a way out of the difficulty, for we can make use of a null method which has already proved of value in a similar problem [5]. The method is in principle very simple and relies on the fact that the intensity distribution in these bands is known [4]. We have thus only to pick out lines in the B-band having the same intensity as lines in the A-band. Then

$$p_{00}\, i_A e^{-\frac{E_A}{kT}} = p_{01} i_B e^{-\frac{E_B}{kT}} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and since everything is known but p_{00}/p_{01} the ratio is determined. Since lines of *equal* intensity are required we may use as a criterion of equality any property of the line which varies unambiguously with the intensity. It is convenient to use for this purpose the total absorption $A = \int_0^\infty A_\nu . d\nu$ of the line, for this is a quantity which is independent of the resolving power of the recording instrument, so that questions of dispersion, slit-width, etc., do not arise.

The lines chosen for the comparison were those of the branches P_2 and P_3, from $P_2(0)$ to (30) in the case of the A-band, and in the B-band from $P_2(0)$ to (24). The stronger lines of the A-band were so broadened that $P_2(J)$ and $P_3(J)$ were merged into one. They have therefore been measured as one; for the remaining lines the absorption of $P_2(J)$ was added to that of $P_3(J)$, and in the remainder of this paper this will be referred to simply as the absorption of P(J). The R-branches were useless for the comparison, as in the A-band the rotational structure had entirely disappeared. It should also be mentioned that the A-band overlays a much fainter band due to the $0_{16}0_{18}$ molecule; where it was possible to do so these fainter lines were neglected. Where they are included (in the stronger lines of the A-branch) their contribution to the absorption is negligible and does not enter into the final results. The transparent scales already referred to, with abscissae in wave-number

units and ordinates in arbitrary intensity units, were placed on the records and the total absorption evaluated for each line. As a check the process was repeated and the mean of the two sets taken. Finally, the values were reduced to a common background intensity of unity, and have been collected together in Table I. We are now in a position to compare these values with one another by means of the calculated distribution. Intensities in the P_2-branch are distributed according to the expression $P_2(J) = \frac{1}{2}(J+2)\exp.(-E/kT)$ and for the P_3-branch

TABLE I.

Lines.	Intensity (calc.).	Measured total absorption.		Calculated total absorption.	
	Arb. units.	B-band.	A-band.	A-band*.	B-band†.
P(0).....	5·28	0·517	2·60	1·75	0·49
P(2).....	16·01	1·21	4·79	4·28	1·20
P(4).....	22·75	1·37	5·28	5·12	1·43
P(6).....	26·17	1·48	5·51	5·50	1·54
P(8).....	26·20	1·53	5·43	5·51	1·54
P(10).....	23·61	1·48	5·12	5·23	1·46
P(12).....	19·54	1·24	4·31	4·76	1·33
P(14).....	14·77	1·01	3·50	4·14	1·16
P(16).....	10·42	0·91	3·32	3·48	0·97
P(18).....	6·88	0·76	2·86	2·82	0·79
P(20).....	4·33	blend	2·18	2·24	0·63
P(22).....	2·50	0·47	1·60	1·70	0·48
P(24).....	1·36	0·36	1·29	1·25	0·35
P(26).....	0·68	—	0·89	0·89	—
P(28).....	0·33	—	0·60	0·62	—
P(30).....	0·15	—	0·43	0·41	—

* These values have been calculated from measurements of α made with 13·70 metres of air (reference 4).

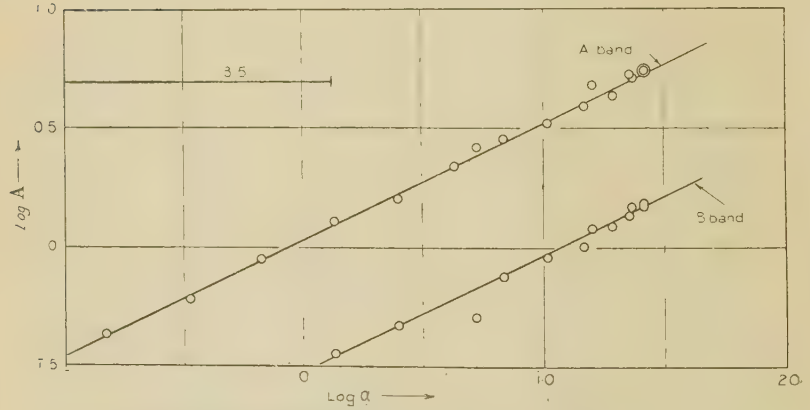
† These values are derived from those of the previous column, making use of the measured intensity ratio of 13·5 : 1.

according to $P_3(J) = \frac{1}{2}(J+\frac{1}{2})\exp.(-E/kT)$. These expressions contain the temperature, so that it would seem at first sight as though the temperature gradient of the atmosphere would need to be taken into account. It will be shown in the next section that this is not so, and that it is sufficient if we replace T in the above expressions by T_0, the ground temperature. The intensity distribution for the P-branches calculated in this way is given in Table I., where, as before, $P(J) = P_2(J) + P_3(J)$.

The actual comparison of the A- and B-bands is most conveniently made by plotting the logarithm of the measured total absorption against the logarithm of the calculated intensity; the points for the B-band should fall on a curve parallel with that of the A-band *, the distance between the two curves being the logarithm of the relative intensities, *i. e.*, $\log p_{00}/_{01}$. This procedure has been followed in fig. 2, from which it will be seen that the two curves are indeed strictly parallel, and that $\log p_{00}/p_{01} = 1{\cdot}13$ so that

$$p_{00}/p_{01} = 13{\cdot}5.$$

Fig. 2.



Total absorption (measured) plotted against intensity (arbitrary units) from Table I. The horizontal distance between the two curves gives the relative intensities of the bands, whilst the slope (0·49) shows that the total absorption varies as the square-root of the number of absorbing centres.

This value needs two corrections: (*a*) a frequency correction, due to the fact that the quanta absorbed are not quite the same for both bands, (*b*) a correction for the slightly different path lengths. Correction (*a*) is applied by multiplying the observed ratio by ν_{01}/ν_{00}, where ν_{01}, ν_{00} are the mean frequencies of the B- and

* It will probably be remarked that this statement is not quite true unless $P_2(J)$ and $P_3(J)$ are of equal intensity. However, for all except the first two lines, the two branches are of so nearly equal intensity (see Pl. XXVIII.) that the methods adopted in this paper of dealing with the added total absorptions P(J) are quite valid.

A-bands respectively. Correction (*b*) follows from the theoretical developments of the next section, and is applied by multiplying the observed ratio by sec δ_B/sec δ_A where δ_B and δ_A are the mean zenith distances of the sun during the respective exposures. Correction (*a*) amounts to 1·11 (*b*) to 0·83, so that the final corrected value of the ratio is

$$p_{00}/p_{01} = 12{\cdot}4.$$

The absolute value of the integrated absorption coefficient for the whole A-band is known to be approximately $3{\cdot}8 \times 10^7$ cm.$^{-1}$/sec.$^{-1}$; the corresponding value for the B-band is therefore $3{\cdot}1 \times 10^6$ cm^{-1} /sec.$^{-1}$. These two bands, therefore, account for the major part of the $^3\Sigma \rightarrow {}^1\Sigma$ transition, with a total intensity of approximately $4{\cdot}1 \times 10^7$ cm.$^{-1}$/sec.$^{-1}$. This corresponds to an electronic transition probability of 0·10 *or a mean life of the* $^1\Sigma$ *state of* 10 *seconds.*

We may compare this value of p_{01} with that of p_{11}[6], found by a comparison of the A-band with its much fainter neighbour A_{11} (vibrational quantum number jump 1→1). When allowance has been made for the much smaller population of the $v'' = 1$ state compared with that of the $v'' = 0$ state, it is found that the A_{00}- and A_{11}-bands have almost equal intensities—in fact, $p_{00}/p_{11} = 1{\cdot}0/0{\cdot}8$. Thus

$$p_{00} : p_{11} : p_{01} = 1{\cdot}0 : 0{\cdot}8 : 0{\cdot}081.$$

When these probabilities are considered in conjunction with the relative populations of the initial vibrational states it will be seen that there is small hope of further additions of new bands to this system. According to the Condon theory of vibrational transition probabilities we should expect to find for a molecule such as oxygen, for which the molecular forces are sensibly the same in both initial and final states, that the transitions 0→0, 1→1, 2→2, etc., have the greatest probability, so that these measured values are entirely consistent with theory.

Total Absorption as a Function of the Number of Absorbing Molecules.

The B-band has recently been the subject of an investigation by Woolley[7], who, by photographing the band at various heights of the sun above the horizon,

endeavoured to verify that the width of an absorption line is proportional to the square root of the number of absorbing molecules. It was expected that the width of a line would be proportional to the square root of sec. δ(δ is the sun's zenith distance), but Woolley found instead a proportionality to the three-eighths power. On the basis of this result he questioned the validity of the square-root law [8], a law which is in astrophysics of fundamental importance for determinations of solar and stellar atomic concentrations, and suggested that deviations from the law might explain certain observed anomalous multiplet intensities. These conclusions were subsequently criticised by Unsöld [9], who pointed out that in all probability Woolley's assumption that the instrumental line width was small compared with the real width is untenable, and that, consequently, the measured widths, especially of the weaker lines, are likely to be much in error and may not be applied without correction to a test of the square-root law. Subsequent evidence for the law has been provided by the success with which, in the hands of Minnaert and Mulders [10], [11] it has explained peculiarities of the Adams-Russell calibration of the Rowland scale of Fraunhofer line intensities.

It is therefore of interest to consider the bearing which the measurements of this paper have upon the problem, for, as already pointed out, they are independent of resolving power and are thus admirably suited to a test of the law. There is every reason for believing that the natural width, *i. e.*, the range of frequencies absorbed by a single undisturbed molecule, of these oxygen lines is extremely small. The Doppler width at ordinary temperatures is also small, and practically the whole of the observed width is due to impact broadening. By impact broadening is meant the broadening consequent upon the abrupt changes of phase the molecule experiences at the impacts of those surrounding it. The shape of the line is thus decided by the number of impacts per second, and may be calculated with the aid of the kinetic theory of gases. Suitable expressions have been obtained by Dennison [12], who has tested them on the infra-red bands of HCl and finds them in reasonably good agreement with the measurements. The expression which we

shall use for the shape of the line is taken from his paper (No. 1″), and with a slightly altered notation becomes

$$\alpha_\nu = \frac{1}{1{\cdot}785\, n\sigma^2\sqrt{kT/m} + \dfrac{2{\cdot}91(\nu-\nu_0)^2}{n\sigma^2\sqrt{kT/m}}} \cdot \alpha \quad . \quad . \quad (2)$$

Here n is the number of molecules per c.c. and σ is the molecular diameter. This diameter is, of course, determined by the nearest distance to which two molecules can approach without an appreciable phase change taking place; Dennison finds for HCl a value roughly twice as large as that deduced from viscosity measurements, a result which he attributes to the strongly polar nature of the molecule. With oxygen diluted with nitrogen on the contrary we shall expect to find a much closer agreement. The other symbols in (2) have their usual significance. Equation (2) holds for the wings of the line; with slightly different numerical constants it applies also to the centre. There is no point in using the two, however; the lines are so strong that to use (2) for the whole line makes no difference to the result.

We can apply this expression immediately to the special case of the atmosphere. It is clear that the shape of the line will be a function of the height. So, too, will the number of molecules per c.c., as well as the distribution of the molecules over the rotational levels of the initial state, for the Boltzmann factor also varies with the height. To save unnecessary complication, the absorption will be treated as though it were a property of the entire atmosphere, and not of the oxygen molecules alone, and the value of α in (2) will be correspondingly adjusted to about one-fifth of its proper value. This is, of course, quite legitimate, and makes no difference to the final result. To integrate (2) over the total light-path, we introduce α', the mean integrated absorption coefficient per molecule, and the Boltzmann factor correction term, and express T and n as functions of the height. For our purpose it is sufficient to make the usual assumption of a linear temperature gradient of 6·5° C. per kilometre, so that

$$T = T_0(1-\epsilon x) \quad ; \quad n = n_0(1-\epsilon x)^{5\cdot 3},$$

where $\epsilon = 2{\cdot}2 \times 10^{-7}$ and x is in cm., and T_0 and n_0 are the ground values. Slight re-arrangement then gives

$$\alpha_\nu = \frac{0{\cdot}56 e^{\frac{E}{kT_0}}}{\sigma^2 \sqrt{kT_0/m}} \alpha' \sec \delta \cdot \int \frac{e^{-\frac{E}{kT_0(1-\epsilon x)}} (1-\epsilon x)^{-3/2}}{1 + \frac{1{\cdot}63\, m}{n_0^2 \sigma^4 kT_0 (1-\epsilon x)^{11{\cdot}6}} (\nu - \nu_0)^2} dx \quad . \quad (3)$$

for the effective value of α_ν for a zenith distance δ. The integration extends from ground level to a height of 45·5 kilometres. Upon giving the constants of (2) the following numerical values :—

$$n_0 = 25 \times 10^{18} \; ; \; \sigma = 2{\cdot}7 \times 10^{-8} \text{ cm.} \; ; \; m = 53 \times 10^{-24} \text{ gm.}$$
$$k = 1{\cdot}37 \times 10^{-16} \text{ ergs/degree,}$$

we obtain

$$\alpha_\omega = 2{\cdot}78 \times 10^{10} \alpha' \sec \delta \, e^{\frac{E}{kT_0}} \int \frac{e^{\frac{-E}{kT_0(1-\epsilon x)}} (1-\epsilon x)^{-3/2}}{1 + \frac{5{\cdot}77 \times 10^3}{(1-\epsilon x)^{11{\cdot}6}} \omega^2} dx \quad (4)$$

where $\omega = (\nu - \nu_0)$ measured in cm.$^{-1}$ units. For small values of ω, (4) must be integrated graphically ; the lines under consideration are so strong, however, that we make no error in the total absorption if we neglect the 1 in the denominator and use the approximate form

$$\alpha_\omega = 4{\cdot}82 \times 10^6 \frac{\alpha' \sec \delta \, e^{\frac{E}{kT_0}}}{\omega^2} \int e^{-\frac{E}{kT_0(1-\epsilon x)}} (1-\epsilon x)^{10{\cdot}1} \, dx. \quad . \quad (5)$$

Upon examination it will be found that this can be still further simplified ; the E values for all the lines under consideration are so small that the variation of the exponential term is negligible compared with that of the bracket term. The exponential term may therefore without error be assumed to have the constant value $e^{-\frac{E}{kT_0}}$, *i. e.*, the Boltzmann factor correction is unnecessary. This is really not surprising. The lines are so strong and broad that the main contribution to the total absorption is provided by relatively large values of ω. But molecules capable of absorbing these frequencies are only appreciable at low altitudes, and are negligibly few at heights where the temperature gradient has had time to change the Boltzmann factor.

It is only when the absorption is small that the contribution of the upper layers becomes important and it is necessary to introduce the correction. This is the justification for the procedure in the first section

With these simplifications (5) can be integrated directly, giving as the result

$$\alpha_\omega = \frac{1{\cdot}97 \times 10^{12}}{\omega^2} \alpha' \sec \delta. \quad . \quad . \quad . \quad . \quad (6)$$

This is the effective absorption coefficient for the whole atmosphere. The total absorption for the whole line is then

$$A = \int_{-\infty}^{+\infty} (1 - e^{-\alpha_\omega}) d\omega, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

or what is practically the same thing, equal to twice the integral between the limits 0 and $+\infty$. As a final result we obtain

$$A = 4{\cdot}98 \times 10^6 (\alpha' \sec \delta)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

We see that for a given line A varies as $(\sec \delta)^{\frac{1}{2}}$, which is exactly equivalent to the relationship tested by Woolley, as is clearly seen from (6). Or if δ is kept constant, A varies as $(\alpha')^{\frac{1}{2}}$. This second conclusion can be checked at once from fig. 2, for there, since we have plotted * log A against log α', we should obtain a straight line of slope 0·5. The actual value in the diagram is 0·49, so that we may conclude that (8) is correct, and that Woolley's suspicions of the validity of the square-root law are unfounded.

As a final test we may compare the measured values of A with those calculated from (8). We may do this by making use of the absolute values of α derived from measurements (see reference 4 for details) on 13·70 metres of air. This is indeed a drastic test of the theory, for it amounts to an extrapolation of measurements made on 13·7 metres of air to a sheet *some* 50 *kilometres thick.* The agreement is astonishingly good ; the calculated values are all a little high, and much of this is no doubt due to the difficulty of making accurate measurements of α, but it must also be remembered that the value assumed for the effective molecular diameter was somewhat arbitrarily taken to be that given by viscosity

* See fig. 2, p. 1054.

measurements. By taking for σ a value of 2·51 instead of $2{\cdot}7 \times 10^{-8}$, we obtain the values of A shown in Table I. No better agreement could be wished. We have here a complete experimental verification of Dennison's line-width formula.

Summary.

Total absorption measurements have been made on the atmospheric A- and B-bands, due to oxygen, with the sun approximately 9° above the horizon. The relative intensities of the bands give directly the ratio of the probabilities (p) of the vibration quantum number transitions, and in this case is found

$$p_{00} : p_{01} = 1 : 0{\cdot}081.$$

Assuming that the whole width of these lines is due to impact broadening, it is possible to calculate the total absorption for any thickness of gas. This has been done for the atmosphere; the calculated values are in excellent agreement with observation. Two consequences of impact broadening are (*a*) the half-width of a line is proportional to the square root of the number of absorbing molecules; (*b*) the total absorption is also proportional to the square-root of the number of absorbing molecules. The measurements of this paper enable conclusion (*b*) to be tested; it is found to be completely verified by both bands.

The writer is indebted to the Director and Managers of the Royal Institution for the opportunity they have provided to undertake this work.

References.

(1) R. M. Badger and R. Mecke, *Zeits. f. Phys.* lx. p. 59 (1930).
(2) R. S. Mulliken, Phys. Rev. xxxii. p. 880 (1928).
(3) R. Schlapp, Phys. Rev. xxxix. p. 806 (1932).
(4) W. H. J. Childs and R. Mecke, *Zeits. f. Phys.* lxviii. p. 344 (1931).
(5) R. Mecke and W. H. J. Childs, *Zeits. f. Phys.* lxviii. p. 362 (1931).
(6) R. Mecke and W. Baumann, *Zeits. f. Phys.* lxxiii. p. 139 (1932).
(7) R. v. d. R. Woolley, Astrophys. Journ. lxxiii. p. 185 (1931).
(8) R. v. d. R. Woolley, Astrophys. J. lxxiii. p. 194 (1931).
(9) A. Unsold, Astrophys. Journ. lxxv. p. 106 (1932).
(10) M. Minnaert and G. F. W. Mulders, *Zeits. f. Astrophys.* i. p. 192 (1930).
(11) M. Minnaert and G. F. W. Mulders, *Zeits. f. Astrophys.* ii. p. 165 (1931).
(12) D. M. Dennison, Phys. Rev. xxxi. p. 511 (1928).

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CIX. *Some Problems concerned with Inverted Prolate Spheroids.* *By* D. M. Wrinch, *M.A., D.Sc.(Oxon.), Hestha Ayrton Fellow, Girton College, Cambridge, and Suzette Taylor Fellow, Lady Margaret Hall, Oxford* *.

§ 1. *Prolate Spheroidal Coordinates.*

PROLATE spheroidal coordinates (μ, ν) have been introduced in the form

$$z = a\mu\nu, \qquad \rho = a(1-\mu^2)^{1/2}(\nu^2-1)^{1/2}.$$

If the origin is moved to a point O on the axis, say $\mu=-1$, $\nu=\nu_0$, we have a new coordinate

$$Z = z + a\nu_0 = a(\mu\nu + \nu_0),$$

and taking O as the centre of inversion and $k=\sqrt{aa'}$ as the radius of inversion, we introduce inverted coordinates Z', ρ' in the form

$$Z' = k^2 Z/R^2, \quad \rho' = k^2\rho/R^2,$$

where R, the distance from O, is

$$a\left((\mu\nu+\nu_0)^2 + (1-\mu^2)(\nu^2-1)\right)^{\frac{1}{2}}$$
$$= a\left[\mu^2+\nu^2+\nu_0^2+2\mu\nu\nu_0-1\right]^{1/2},$$

and R′, the distance of the inverted point from the origin is k^2/R.

The space elements normal to the μ and ν levels are now

$$\delta n_\mu = \delta\mu/h_\mu', \qquad \delta n_\nu = \delta\nu/h_\nu',$$

with

$$\frac{h_\mu'}{h_\mu} = \frac{h_\nu'}{h_\nu} = \frac{R}{R'} = \frac{k^2}{R'^2} = \frac{R^2}{k^2}.$$

Thus

$$h_\nu'^2 = k^2 h_\nu/R'^2$$
$$= \left(\frac{\nu^2-1}{\nu^2-\mu^2}\right)^{1/2} \frac{a'}{R'^2},$$

so that

$$\frac{\partial}{\partial n_\nu} = h_\nu' \frac{\partial}{\partial\nu} = \left(\frac{\nu^2-1}{\nu^2-\mu^2}\right)^{1/2} \frac{a'}{R'^2} \frac{\partial}{\partial\nu}.$$

The surfaces given by $\mu=$constant are the inverses of the hyperboloids, which are the μ-levels in the original coordinates. Similarly, the ν-levels in these new coordinates

* Communicated by the Author.

are the inverses of the ν-levels in the original coordinates, namely, the prolate spheroids.

§ 2. *The Inverted Spheroids.*

The inverse of a prolate spheroid $\nu=\nu_1$ will be of two types, according to whether the centre of inversion lies outside the spheroid—which is the case when $\nu_0>\nu_1$—or inside the spheroid—which is the case when $\nu_0<\nu_1$.

The prolate spheroid $\nu=\nu_1$ has equation

$$\frac{\rho^2}{a^2(\nu_1^2-1)}=1-\frac{(Z-a\nu_0)^2}{a^2\nu_1^2}=\frac{z_1z_2}{a^2\nu_1^2},$$

where z_1, z_2 are the distances from the points $z=\pm a\nu_1$. Thus the inverted surface ν_1 has equation

$$\frac{k^4\rho'^2}{a^2(\nu_1^2-1)R'^4}=1-\frac{[k^2Z'/R'^2-k^2\nu_0/a']^2}{a^2\nu_1^2}$$

or

$$\rho'^2=\frac{\nu_1^2-1}{\nu_1^2a'^2}[\nu_1R'^2-Z'a'+\nu_0R'^2][\nu_1R'^2+Z'a'-\nu_0R'^2]$$

$$=\frac{(\nu_1^2-1)(\nu_0^2-\nu_1^2)}{\nu_1^2a'^2}\left[R'^2-\frac{Z'a'}{\nu_1+\nu_0}\right]\left[\frac{Z'a'}{\nu_0-\nu_1}-R'^2\right].$$

The ends of the major axis of this surface are at

$$Z'=\frac{a'}{\nu_0\pm\nu_1},$$

so that the major axis is of length $2\nu_1a'/(\nu_0^2-\nu_1^2)$. Further, the curvature at the ends of the major axes, which are respectively nearer and further from the centre of inversion, are c_1 and c_2, given by

$$\frac{1}{c_1}=\lim_{\rho'=0}\frac{\rho'^2}{2(Z'-a'(\nu_1+\nu_0))}$$

$$=\frac{(\nu_1^2-1)(\nu_1^2-\nu_0^2)}{2\nu_1^2a'^2}\left(\frac{a'}{\nu_1+\nu_0}\right)^2\left[\frac{a'}{\nu_0-\nu_1}-\frac{a'}{\nu_1+\nu_0}\right]$$

$$=\frac{(\nu_1^2-1)a'}{\nu_1(\nu_1+\nu_0)^2},$$

$$\frac{1}{c_2}=\frac{(\nu_1^2-1)a'}{\nu_1(\nu_0-\nu_1)^2},$$

It will be remarked that $c_2<c_1$ and that

$$\frac{c_1}{c_2}=\left(\frac{\nu_0+\nu_1}{\nu_0-\nu_1}\right)^2.$$

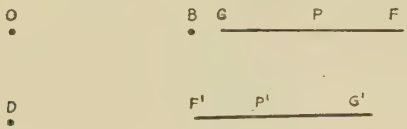
§ 3. *The Asymmetric Rod.*

It is one of the interesting features of prolate spheroids that the limiting form when ν_1 tends to unity, is an asymmetric rod. Its length is $2a'/(\nu_0^2-1)$ and its equation is

$$\frac{\rho'^2}{(\nu_1^2-1)_{\nu_1=1}} = \frac{\nu_0^2-1}{a'^2} Z'^2\left(Z'-\frac{a'}{\nu_0+1}\right)\left(\frac{a'}{\nu_0-1}-Z'\right)$$
$$= \frac{\nu_0^2-1}{a'^2} Z'^2 z_1' z_2',$$

where z_1' and z_2' are the distances of a point on it from F', G', the ends of the rod, *i. e.*, the points nearest and furthest from the centre of inversion. The asymmetry of the rod may therefore be indicated by saying that its thickness at any point P' on it is proportional to $OP' \times \sqrt{(F'P'.P'G')}$. By suitably varying the origin O we could consequently obtain a large variety of asymmetric rods, whose thicknesses are proportional to the geometric mean of the distances from

Fig, 1.



the ends (as in the case of the spheroidal rod) multiplied by the distance from any fixed external point on its axis. Since the curvatures at the ends of the rod are in the ratio

$$\frac{c_1}{c_2} = \left(\frac{\nu_0+1}{\nu_0-1}\right)^2 = \left(\frac{OG'}{OF'}\right)^2 = \left(\frac{OG}{OF}\right)^2,$$

the point O may be selected so as to obtain any specified ratio between the curvatures. Thus we may obtain rods which have one end as much blunter than the other as we choose.

Thus, for example, we may consider a series of asymmetric rods ranging from the case when the curvatures at the ends are nearly equal through the cases when

$$\nu_0 = 5,\ 3,\ 2,\ 1{\cdot}5\ \ldots,$$

and

$$c_2/c_1 = 4/9,\ 1/4,\ 1/9,\ 1/25,\ \ldots,$$

corresponding to

$$OG/OF = OF'/OG' = 2/3,\ 1/2,\ 1/3,\ 1/5,\ \ldots,$$

to the extreme case when by taking $\nu_0 - \nu_1 = \epsilon$ and $\nu_1 - 1 = \eta$, where ϵ and η are of the same order of smallness, we get a rod whose curvatures are given by

$$\frac{1}{c_1} = \frac{\eta a'}{2}, \qquad \frac{1}{c_2} = \frac{2\eta a'}{\epsilon},$$

so that one end has zero curvature and the other infinite curvature, and the rod resembles a nail.

§ 4. *The ϕ and ψ-functions for Inverted Prolate Spheroidal Coordinates.*

To find suitable forms for the potential function ϕ and for the associated ψ-function in the new inverted coordinates, it is not necessary to refer to the general equation for ϕ',

$$\left[\frac{\partial}{\partial\mu}\frac{h_\mu'}{h_\nu' h_\omega'}\frac{\partial}{\partial\mu} + \frac{\partial}{\partial\nu}\frac{h_\nu'}{h_\omega' h_\mu'}\frac{\partial}{\partial\nu} + \frac{\partial}{\partial\omega}\frac{h_\omega'}{h_\mu' h_\nu'}\frac{\partial}{\partial\omega}\right]\phi' = 0,$$

and the corresponding equation for ψ', and solve directly. For, having the solution,

$$\phi = \Sigma a_{m,n} \cos m\omega \left[\mathrm{P}_n^m(\mu), \mathrm{Q}_n^m(\mu)\right]\left[\mathrm{P}_n^m(\nu), \mathrm{Q}_n^m(\nu)\right],$$

for our original coordinates, we have at once the solution

$$\phi' = \left(\frac{\mathrm{R}}{a}, \frac{a'}{\mathrm{R}'}\right)\phi$$

by means of the general theorem for inversion. Thus we have ready to hand ϕ-functions for problems associated with inverted spheroids of the same generality as the potential functions already obtained for problems connected with spheroids These functions will also have corresponding properties.

We shall consider only cases when there is symmetry about the axis of figure. Thus we may take

$$\phi' = \left(\frac{\mathrm{R}}{a}, \frac{a'}{\mathrm{R}'}\right)\phi,$$

where

$$\phi = \sum_0^\infty a_n \mathrm{P}_n(\mu)\mathrm{P}_n(\nu),$$

and, in the case when $\nu_0 > \nu_1$, obtain a potential function ϕ' without singularities within the inverted spheroid ν_1. Similarly, taking

$$\phi = \sum_0^\infty a_n \mathrm{P}_n(\mu)\mathrm{Q}_n(\nu),$$

which is a potential function without singularities outside the spheroid ν_1, we have, when still $\nu_0 > \nu_1$,

$$\phi' + \left(\frac{R}{a}, \frac{a'}{R'}\right) \sum_0^\infty a_n P_n(\mu) Q_n(\nu),$$

as a potential function without singularities outside the inverted spheroid ν_1, except possibly at the point $R'=0$. But consider the value of ϕ' as R' tends to zero. We have

$$\lim_{R'=0} (\phi' R') = \lim_{R=\infty} (a'\phi).$$

But on the sphere at infinity $R=\infty$, ϕ is at most of order $1/R$. Therefore ϕ' as R' tends to zero is certainly finite.

In the alternative case, when $\nu_0 < \nu_1$, the suitable forms for the potential ϕ' interchange. When $\nu_0 > \nu_1$ the insides of the spheroid ν_1 and of the inverted spheroid ν_1 correspond: also the regions outside. When $\nu_0 < \nu_1$ the inside of the one corresponds to the region outside the other. Thus, with $\nu_0 < \nu_1$, the form is suitable for the domain outside the inverted spheroid ν_1 and the form for the domain inside, and in all cases where there is symmetry about the axis of figure,

$$\phi' = \frac{a'}{R'} \sum_0^\infty [a_n P_n(\nu),\ b_n Q_n(\nu)] P_n(\mu).$$

Now just as we have the relation

$$\phi' = \frac{a'}{R'} \phi$$

between potential functions for a set of coordinates and their inverses, so we have the relation

$$\psi' = \frac{R'}{a'} \psi.$$

Thus, corresponding to

$$\psi = \sum_0^\infty (1-\mu^2) P_n'(\mu) [C_n(\nu^2-1) P_n'(\nu),\ D_n(\nu^2-1) Q_n'(\nu)],$$

we can take

$$\psi' = \frac{R'}{a} \sum_0^\infty (1-\mu^2) P_n'(\mu) [C_n(\nu^2-1) P_n'(\nu),\ D_n(\nu^2-1)(Q_n'(\nu)].$$

§ 5. *Typical Applications in Electrostatics.*

5·1. We may first discuss the problem of an inverted spheroidal conductor ν_1 earthed under the influence of a

point charge $-E'$ at B′, an external point on its axis, B′ being the inverse of the point B given by $\mu=-1$, $\nu=\nu_2$, the case when B coincides with O, the centre of inversion being excluded. We will take O to be external to the original spheroid $\nu=\nu_2$, so that $\nu_0>\nu_2$. We, further, have $\nu_2>\nu_1$, for B′ is external to the inverted spheroid $\nu=\nu_1$ and, in consequence, B is external to the spheroid $\nu=\nu_1$. Also, $\nu_2\neq\nu_0$.

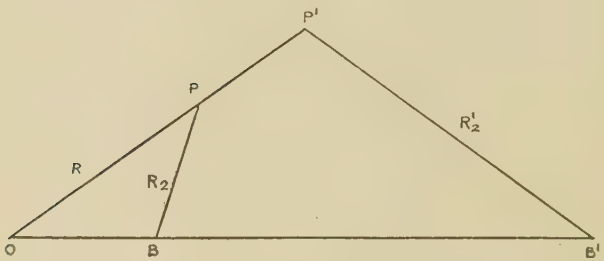
A suitable form for the potential thrown off by the conductor is

$$V_1' = \frac{R}{a} V_1 = \frac{a'}{R'} V_1,$$

where

$$V_1 = \sum_0^\infty a_n P_n(\mu) Q_n(\nu).$$

Fig. 1.



Further, the potential of the point charge $-E'$, alone in space, is

$$V_2' = -E'/R_2' = a'V_2/R'$$

if

$$V_2 = -\frac{E'}{a'} \cdot \frac{R'}{R_2'},$$

R_2 being written for the distance of a point P from B, and R_2' for the distance of the inverse point P′ from B′. But referring to fig. 1, we have

$$\frac{R_2'}{R_2} = \frac{P'B'}{PB} = \frac{OP'}{OB} = \frac{OB'}{OP} = \frac{k^2}{OB.OP} = \frac{OB'.OP'}{k^2}.$$

Therefore

$$\frac{R_2'}{R_2} = \frac{R'}{OB} = \frac{OB'}{R}$$

and

$$V_2 = -\frac{E}{R_2}$$

if

$$\frac{E'}{E} = \frac{a'}{OB} = \frac{OB'}{a} = \frac{a'}{a(\nu_0-\nu_2)}.$$

Thus V_2 is manifestly the potential of a corresponding point charge $-E$ at the point B inverse to B'.

Now we have to choose the potential V_1' thrown out by the inverted spheroidal conductor in such a manner that $V_1'+V_2'$ is zero on the conductor. Hence, if V_1 is so chosen that V_1+V_2 is zero on the original spheroidal conductor $\nu=\nu_1$, the conditions of the problem are satisfied. Thus we are, in fact, taking the solution of the problem of the spheroidal conductor under the influence of a point charge $-E$ at B and using it to solve the problem of the inverted spheroidal conductor under the influence of a point charge $-E'$ at B'.

Now

$$V_2 = -E/a\,[(\mu\nu+\nu_2)^2+(1-\mu^2)(\nu_2-1)]^{1/2}$$

$$= -\frac{E}{a}\sum_0^\infty (-)^n(2n+1)P_n(\mu)P_n(\nu)Q_n(\nu_2), \quad (\nu<\nu_2).$$

Hence, writing

$$V_1 = \frac{E}{a}\sum_0^\infty (-)^n(2n+1)P_n(\mu)\frac{P_n(\nu_1)Q_n(\nu_2)}{Q_n(\nu_1)}Q_n(\nu),$$

we have (V_1+V_2) zero on $\nu=\nu_1$.

To find σ', the surface density of electrification, we have, if σ be the surface density of electrification in the corresponding problem relating to the spheroid ν_1,

$$4\pi\sigma' = -\frac{\partial}{\partial n_\nu'}(V_1'+V_2') = -\frac{a'}{R'}\frac{\partial}{\partial n_\nu'}(V_1+V_2)_{\nu=\nu_1},$$

so that

$$\frac{\sigma'}{\sigma} = \frac{a'}{R'}\frac{h_\nu'}{h_\nu} = \frac{a'}{R'}\cdot\frac{k^2}{R'^2} = \frac{R^3}{ak^2} = \left(\frac{a'R^3}{aR'^3}\right)^{1/2}.$$

Thus we have, in fact,

$$4\pi\sigma = \frac{E'(\nu_0-\nu_2)\,a'/R'^3}{(\nu_1^2-\mu^2)^{1/2}(\nu_1^2-1)^{1/2}}\sum_0^\infty (-)^n(2n+1)P_n(\mu)\frac{Q_n(\nu_2)}{Q_n(\nu_1)}.$$

Furthermore, the total charge induced on the conductor is e', where

$$e' = \lim_{R'=\infty}(V_1'R_1') = \lim_{R=0}(a'V_1) = \lim_{\mu=-1,\ \nu=\nu_0}(a'V_1)$$

$$= \frac{Ea'}{a}\sum_0^\infty (-)^n(2n+1)P_n(-1)P_n(\nu_1)Q_n(\nu_2)\,Q_n(\nu_0)/Q_n(\nu_1).$$

$$= E'(\nu_0-\nu_2)\sum_0^\infty (2n+1)P_n(\nu_1)Q_n(\nu_2)\,Q_n(\nu_0)/Q_n(\nu_1).$$

This series allows simple approximations when ν_0 and/or ν_2 are sufficiently big.

The case when ν_1 tends to unity and the inverted spheroid approximates to a thin asymmetric rod is also of interest. The solution of the problem is available directly from the corresponding problem relating to the symmetric rod earthed under the influence of a charge at B. Thus, since

$$\frac{1}{\sigma} \propto (2+a\nu_2)(a^2-z^2)^{1/2} = \mathrm{BP}(\mathrm{GP}.\mathrm{PF})^{1/2},$$

we deduce

$$\frac{1}{\sigma'} \propto a.\mathrm{BP}(\mathrm{GP}.\mathrm{PF})^{1/2}/\mathrm{OP}^3$$

$$\propto \mathrm{P'B'}.(\mathrm{F'P'}.\mathrm{P'G'})^{1/2}.\mathrm{OP'} \propto \rho' \cdot \mathrm{P'B'},$$

since for the asymmetric rod

$$\rho' \propto \mathrm{OP'}(\mathrm{F'P'}.\mathrm{P'G'})^{1/2}.$$

The way in which this result is stated is interesting, since it shows how the distribution of electricity depends on the asymmetry of the rod and also on the position of the charge. Incidentally, we may remark, since

$$\sigma' \propto 1/\rho'\left(\frac{a'}{\nu_0-\nu_2} - \mathrm{Z'}\right),$$

that

$$\sigma'_{\mathrm{F'}}/\sigma'_{\mathrm{G'}} = \frac{\nu_2-1}{\nu_0-1} \cdot \frac{\nu_0+1}{\nu_2+1} \cdot \frac{\mathrm{O'G'}}{\mathrm{O'F'}} = \left(\frac{\nu_0+1}{\nu_0-1}\right)^2 + \frac{\nu_2-1}{\nu_2+1}.$$

This result indicates the tendency of the sharper end F′ to pick up more electricity than the blunter end G′, being counterbalanced by the fact that the point charge at B_2' is nearer to the blunt end than to the sharp end.

5·2. The problem of an earthed conductor containing a cavity, in the form of an inverted spheroid, there being a point charge at an internal point on its axis, can be attacked in a similar manner. Let the electric charge be $-\mathrm{E}'$, and let it be placed at a point $\mu=-1$, $\nu=\nu_2$. Thus $\nu_2<\nu_1$, and for values of ν between ν_2 and ν_1, we have

$$\mathrm{V}' = \mathrm{V}_2' + \mathrm{V}_1' = \frac{a'}{\mathrm{R}'}(\nu_2+\nu_1)$$

$$= \frac{\mathrm{E}'}{\mathrm{R}'}(\nu_0-\nu_2)\sum_0^\infty (-)^n(2n+1)\mathrm{P}_n(\mu)\mathrm{P}_n(\nu_2)$$

$$\left[\frac{\mathrm{Q}_n(\nu_1)}{\mathrm{P}_n(\nu_1)}\mathrm{P}_n(\nu) - \mathrm{Q}_n(\nu)\right],$$

so that

$$4\pi\sigma = \frac{E'(\nu_0-\nu_2)\,a'/R'^3}{(\nu_1^2-\mu^2)^{1/2}(\nu_1^2-1)^{1/2}} \sum_0^\infty (-)^n(2n+1)P_n(\mu)\frac{P_n(\nu_2)}{P_n(\nu_1)}.$$

5·3. Suppose, now, that the charge $-E$, which is influencing the earthed spheroidal conductor ν_1, is at the point $\mu=-1$, $\nu=\nu_0$—in fact, that $\nu_2=\nu_0$—so that the point charge is at the point subsequently taken as the centre of inversion.

Then if

$$V_1' = \frac{a'}{R'}V_1,$$

where V_1 is the potential thrown out by the earthed conductor ν_1, then on $\nu=\nu_1$,

$$V_1 = \frac{E}{R};$$

consequently, on the inverted spheroidal conductor ν_1,

$$V_1' = \frac{a'}{R'}\cdot\frac{E}{R} = \frac{E}{a}.$$

Thus V_1' is, as is well known, the potential of the conductor formed by the inverted spheroid ν_1, when it is freely charged to potential E/a. Thus the freely-charged inverse conductor with potential $K=E/a$ has potential

$$V_1' = \frac{a'K}{R'}\sum_0^\infty (-)^n(2n+1)P_n(\mu)\frac{P_n(\nu_1)Q_n(\nu_2)}{Q_n(\nu_1)}Q_n(\nu).$$

Further, the surface density σ' is given in terms of σ for the corresponding problem by

$$\frac{\sigma'}{\sigma} = \frac{k^2a'}{R'^3} = \frac{R_3}{k^2a} = \left(\frac{a'R^3}{aR'^3}\right)^{1/2},$$

as usual: and actually

$$4\pi\sigma = \frac{a'^2K/R'^3}{(\nu_1^2-\mu^2)^{1/2}(\nu_1^2-1)^{1/2}}\sum_0^\infty (-)^n(2n+1)\frac{P_n(\mu)Q_n(\nu_0)}{Q_n(\nu_1)}.$$

Finally, the charge e' on the conductor and the capacity c' are given by

$$c' = \frac{e'}{K} = a'\sum_0^\infty (2n+1)\frac{P_n(\nu_1)Q_n^2(\nu_0)}{Q_n(\nu_1)}.$$

In the particular case of the asymmetric rod—when ν_1

tends to unity—we have, when it is freely charged with electricity to potential K,

$$V_1' = \frac{a'K}{R'[Q_0(\nu_1)]_{\nu_1=1}} \sum_0^\infty (-)^n (2n+1) P_n(\mu) Q_n(\nu_0) Q_n(\nu)$$

and

$$\sigma' \propto \frac{R^2}{(a^2-z^2)^{1/2}} \propto \frac{1}{\rho'}.$$

Thus the surface density is inversely proportional to the thickness of the rod at any point. It is also of interest to notice that the capacity of the rod c' is given by

$$\frac{c'}{a'}[Q_0(\nu_1)]_{\nu_1=0} = \sum_0^\infty (2n+1) Q_n^2(\nu_0),$$

a series whose sum is $1/(\nu_0^2-1)$. But the length of the rod is $2a'/(\nu_0^2-1)$, so that the capacities of rods of this type of different lengths, all strictly zero, stand in the ratio of their lengths.

CX. *The Raman Effect in Organic Nitrates.* *By* A. S. Ganesan, *M.A.*, *Ph.D.* (*London*), *D.I.C.*, *and* V. N. Thatte, *M.Sc.* (*College of Science, Nagpur*) *.

[Plate XXIX.]

THE Raman effect in inorganic nitrates has been studied by a number of investigators and it will be interesting to see how far it differs from the effect in organic nitrates. While it is generally recognized that each Raman line in the scattered spectrum of a liquid, or absorption line in its infra-red spectrum, is associated with a normal mode of vibration of a particular group in the molecule or a linkage, it is also well known that these normal modes of vibration are greatly affected by the environment of the group, the restrictions imposed on them depending upon the strength of binding of the other parts of the molecule, and in the case of solutions, by the molecules of the solvent also. Considerable light will thus be thrown on this particular aspect of the question by studying the Raman effect not only of a number of closely-allied compounds, but also of the same compound under different physical conditions.

* Communicated by the Authors.

In the present paper are reported the results of investigation on the scattering by organic nitrates and by alcoholic solutions of some of them. The liquids studied were methyl nitrate, ethyl nitrate, propyl and isopropyl nitrates, isobutyl nitrate and iso-amyl nitrate, and also solutions of methyl nitrate in methyl alcohol and iso-amyl nitrate in iso-amyl alcohol. Methyl, propyl, and isopropyl nitrates were prepared in the laboratory according to the method described by Perkin (Journal of the Chemical Society, p. 683, 1889), for studying the magnetic rotation of these compounds. The other nitrates were obtained from Messrs. Kahlbaum.

TABLE I.

Methyl nitrate.

Modified lines.			Wave-number difference	Infra-red
λ_{air} Å.	Intensity.	$\nu_{vac.}$ cm.$^{-1}$,	$\delta\nu$.	λ (μ).
5005·5	2	19973	2965	3·37
4692·7	2	21304	1634	6·12
4653·4	2 *d*	21484	1454	6·87
4618·1	6	21648	1290	7·75
*4599·3	5	21736	2969	3·37
4571·7	0	21867	1071	9·34
4529·9	4	22069	869	11·5
4488·0	2	22276	662	15·1
4472·4	4	22353	585	17·1

* Excited by λ 4046·6.

The experimental procedure was the same as that adopted by the authors in their previous investigations. The liquids were distilled in vacuum and were contained in Wood's tubes and the source of light was the quartz mercury lamp. The photographs were taken with a Hilger E_3 Quartz Spectrograph on backed iso-zenith plates. The results are collected in Tables I. to VI. Only the modified lines excited by λ 4358·3 (ν 22938 cm.$^{-1}$) of the mercury arc are given in the Tables, though the complete spectrum was measured in each case for the correct allocation of the lines.

Methyl nitrate.—The scattered spectrum in this liquid shows eight Raman lines of which the two corresponding

TABLE II.

Ethyl nitrate.

Modified lines. λ_{air} Å.	Intensity.	$\nu_{vac.}$ cm.$^{-1}$.	Wave-number difference $\delta\nu$.	Infra-red λ (μ).
5010·0	0	19954	2984	3·35
4692·1	2	21307	1631	6·13
4652·4	2 *d*	21488	1450	6·90
4639·1	1 *d*	21550	1388	7·20
4616·3	3	21657	1281	7.81
*4603·4	3 *d*	21717	2988	3·35
*4595·4	3 *d*	21755	2950	3·39
4581·3	1	21822	1116	8·96
4561·5	1	21917	1021	9·79
4528·7	4	22076	862	11·6
4471·0	4	22360	578	17·3
4435·0	2	22542	396	25·2

* Excited by λ 4046·6.

TABLE III.

Propyl nitrate.

Modified lines. λ_{air} Å.	Intensity.	$\nu_{vac.}$ cm.$^{-1}$.	Wave-number difference $\delta\nu$.	Infra-red λ (μ).
4992·5	4	20024	2914	3·43
4981·1	3	20070	2868	3·48
4654·8	5	21478	1460	6·85
4618·2	2 *d*	21647	1291	7·75
*4590·3	3	21779	2926	3·42
*4581·9	2 *d*	21819	2886	3·47
4570·8	2	21872	1066	9·34
4552·5	2	21959	979	10.2
4531·2	4 *d*	22063	875	11·5
*4124·9	1	24236	469	21·3

* Excited by λ 4046·6.

TABLE IV.

Isopropyl nitrate.

Modified lines.			Wave-number difference	Infra-red
λ_{air} Å.	Intensity.	$\nu_{vac.}$ cm.$^{-1}$.	$\delta\nu$.	λ (μ).
5007·6	3	19964	2974	3·36
4991·6	2 *d*	20028	2910	3·44
4983·3	2	20061	2877	3·48
4654·6	3 *d*	21478	1460	6·85
4584·5	2 *d*	21806	1132	8·83
4548·8	2	21977	961	10·4
4520·8	5	22114	824	12·1
4499·6	1	22218	720	13·9

TABLE V.

Isobutyl nitrate.

Modified lines.			Wave-number difference	Infra-red
λ_{air} Å.	Intensity.	$\nu_{vac.}$ cm.$^{-1}$.	$\delta\nu$.	λ (μ).
5005·7	2	19972	2966	3·37
4984·0	2	20059	2879	3·47
4691·4	2	21310	1628	6·14
4656·6	2	21469	1469	6·83
4616·1	2	21657	1281	7·81
*4600·5	5	21731	2974	3·37
*4584·0	5	21809	2896	3·46
4549·1	3	21976	962	10·4
4530·1	3 *d*	22068	870	11·6
4478·4	2	22323	615	16·3
4457·0	1	22431	507	19·8
4441·5	2 *d*	22509	429	23·7
4425·0	1	22593	345	29·0
4408·5	2	22677	261	38·3

* Excited by λ 4046·6.

to frequency-shifts 1454 and 2965 are associated with the oscillations of the CH group. The first line is faint and diffuse, while the second is sharp and single. The weak shift at 1071 is due to the CO linkage, and the structure of this line undergoes the same changes in the nitrates as we go up the series as in the corresponding alcohols. The remaining five frequencies give rise to strong lines, and

TABLE VI.

Iso-amyl nitrate.

Modified lines.			Wave-number difference	Infra-red
λ_{air} Å.	Intensity.	$\nu_{vac.}$ cm.$^{-1}$.	$\delta\nu$.	λ (μ).
5005·8	2	19971	2967	3·37
4984·7	2	20056	2882	3·47
4692·8	2 *d*	21303	1635	6·12
4676·2	0	21379	1559	6·41
4654·1	3 *d*	21480	1458	6·86
4630·5	0	21590	1348	7·42
4616·8	3	21654	1284	7·79
*4599·9	5	21733	2972	3·37
*4581·3	5	21822	2883	3·47
4553·8	1 *d*	21954	984	10·2
4529·7	4	22070	868	11·5
4510·2	1	22166	772	13·0
4473·9	1 *d*	22345	593	16·8
4439·1	1	22520	418	24·0
4413·7	2	22650	288	34·7

* Excited by λ 4046·6.

arranged in the decreasing order of intensities they are 1290, 869, 585, 662, and 1634 cm^{-1}. The infra-red absorption of methyl nitrate has been studied by Plyer and Steele * in the region from 1·0 to 7·5 μ, and prominent absorption bands are observed at 2·96, 4·12, 4·30, 6·02, and 6·74 μ. The first of these bands is evidently due to the CH linkage, but the difference between the infra-red value and the Raman effect value is very great. In this connexion it may be remarked that in methyl alcohol, as also in the other

* Plyer and Steele, Phys. Rev. xxxiv. p. 599 (1929).

alcohols, the discrepancy between the two values is of the same order, the strong infra-red absorption being observed at 3·0 μ, while the Raman shift corresponds to 3·4 μ. The infra-red absorptions 4·12 μ and 4·30 μ are not represented in the Raman effect, while 6·02 μ and 6·74 μ are shifted to the longer wave-length side by about 0·1 μ. The infra-red observation does not go beyond 7·5 μ, and it is doubtful if $\delta\nu$ 1290 will be represented there. However, there are reasons to suppose that this strong shift is probably one of the optically inactive frequencies in the methyl nitrate molecule.

Ethyl nitrate.—The strongest shifts are 578 and 862. The frequency 662 of methyl nitrate is absent here, but instead we get a new shift 396 which is fairly prominent. The longer shifts occupy identical positions as in methyl nitrate. The 3·4 μ band, which is sharp in methyl nitrate, is split up into two, 1021 and 1116, as in ethyl alcohol. In the infra-red absorption, bands occur at 3·02, 4·34, 6·70, and 7·06 μ. Corresponding to the last infra-red absorption wave-length we get the Raman shift at 1388 or 7·20 μ.

Propyl nitrate.—The strongest shift here is 875, which is diffuse. $\delta\nu$ 1460, which is weak in methyl and ethyl nitrates, is very strong in the spectrum of this liquid. $\delta\nu$ 1290, strong in the other spectra, is comparatively weak in this. The band at 3·4 μ is shifted to shorter wave-length side and consists of two components. The infra-red absorptions as observed by Plyer and Steele (*loc. cit.*) are at 3·02, 4·30, 6·70, and 7·06 μ. The characteristic frequency 1630 cm.$^{-1}$, which is conspicuous in the other two spectra, is absent here.

Isopropyl nitrate.—The line corresponding to $\delta\nu$ 824 is the strongest in the scattered spectrum of this liquid. This shift has the lowest value here and is also the sharpest. Frequencies less than 720 cm.$^{-1}$ are not observed, and $\delta\nu$ 1220 is conspicuously absent. $\delta\nu$ 1460 is strong as in propyl nitrate, but more diffuse. The band at 3·4 μ is triple, the outermost component being the strongest.

Isobutyl nitrate.—The spectrum of this liquid is the richest in the series so far as the number of lines are concerned. Many short shifts are observed, the most prominent of these being 261, 429, 615, and 870. The last of these is the strongest and is diffuse towards the violet side, where it has probably a component which is not resolved. The CO

frequency appears at 962 and is single and much more intense than in the other spectra. 3·4 μ band consists of two components that are more diffuse than in the other spectra.

Iso-amyl nitrate.—The Raman effect in this liquid was reported by us in a previous paper *. A fresh spectrogram was taken under more favourable conditions, which has brought out new lines not mentioned in that paper. The prominent lines correspond to frequency differences 868, 1284, 1458, and 1635, of which the first is the strongest. The 3·4 μ band appears as a continuous band with very sharp edges.

General Discussion.

From the above description of the scattering in individual liquids, it is clear that we can divide the observed frequencies in the spectra of organic nitrates into three groups; the first group which has its origin in the oscillations of the CH linkage, the second group associated with the CO linkage, and the third characteristic of the nitrate group. For the purpose of general discussion we shall take these three groups of frequencies one by one.

The CH frequencies.—The two well-known CH frequencies in aliphatic compounds are 1450 and 2940. In aromatic compounds they take the values 1600 and 3050 respectively. Both these frequencies are present in the infra-red spectra as strong absorption bands at 3·0 to 3·4 μ and at 7·0 to 7·2 μ. To understand how these frequencies are affected by the other groups in the molecule, we have shown in Tables VII. and VIII. their values in a number of different compounds. In the first of these tables are given their values in molecules where the alkyl radical is kept the same while the attached group varies; while in the second table are given their values in molecules where the alkyl radical changes, the attached group remaining the same. Figures in brackets show that those frequencies are strong in the corresponding spectrum. One fact which is at once evident is that while the shift 1450 always remains single, structure is exhibited by the longer shift 2940. The only exception is the allyl compound, and this can at once be connected with the unsaturated nature of the compound. The influence of an adjoining group on the normal modes of vibration

* Thatte and Ganesan, Phil. Mag. xii. p. 826 (1931).

of a bond depends not only on the weight of the group but also on the strength of its binding and the polarization of the molecule. These affect some of the normal vibrations to a small extent, while others are affected considerably.

TABLE VII.

CH Frequencies in methyl compounds.

	7 μ.	3·4 μ.
Methyl alcohol $CH_3 . OH$	1465	(2834), (2939)
Acetic acid $CH_3 . COOH$	(1433)	(2943), 2996, 3033
Acetaldehyde $CH_3 . CHO$	1417	2850, (2922), 2997
Methyl mercaptan $CH_3 . SH$.....	1425	2871, (2932), 2975
Aceto-nitrile $CH_3 . CN$	(1364)	(2941)
Nitromethane $CH_3 . NO_2$	(1396)	(2961), 3042
Methyl nitrate $CH_3 . NO_3$.....	1454	2965

TABLE VIII.

CH frequencies in alcohols and nitrates.

	Alcohols.		Nitrates.	
	7 μ.	3·4 μ.	7 μ.	3·4 μ.
Methyl	1465	(2834), (2939)	1454	(2965)
Ethyl	1461	2872, (2930), 2973	1450	(2950), (2988)
Propyl	1464	(2873), (2913), (2945), 2970	(1460)	2886, (2920)
Iso-propyl...	(1454)	(2879), 2919, 2938, (2976)	(1460)	(2877), 2910, (2974)
Isobutyl.....	(1462)	(2874), (2965)	1469	(2879), (2970)
Iso-amyl ...	(1458)	(2880), (2982)	(1458)	(2880), (2967)
Allyl	1419, 1468	2868, 2928, (3014)		

Comparing the CH frequencies in methyl alcohol and methyl mercaptan, the effect of replacing the oxygen atom by the heavier sulphur atom on the shorter frequency is to reduce its value from 1465 to 1425, while on the longer frequency it is to split it into further components. This two-fold influence of the substituted group seems to be general ; the influence on the first CH frequency is to

alter its value and intensity, while that on the second frequency is to alter its structure, the centre of the band remaining almost undisplaced. Whereas the substituted groups alter the value of the shorter shift as shown in Table VII., a mere addition of CH_2 groups produces apparently no change in the value of this shift, as is evident from Table VIII. There is, however, a change in the intensity, the iso-compounds showing the lines stronger than the normal compounds.

The CO frequency.—As already mentioned the frequency 1071 is associated with the CO oscillation. As an additional CH_2 group is added two features appear, viz., the line is split up into further components and their intensities increase. Thus the weak line $\delta\nu$ 1071 of methyl nitrate is split up into two components 1021 and 1116 of a greater intensity in ethyl nitrate, and into three components 979, 1066, and 1119 of a still greater intensity in propyl nitrate. These features are also to be noticed in the respective alcohols, where, however, the intensity does not increase as appreciably as in the case of the nitrates.

The nitrate frequencies.—In this group come the other frequencies not included in the first two groups. Their origin is evidently in the NO_3 group. It must, however, be mentioned that they are not the ionic frequencies which we shall discuss in the following paragraph. Taking methyl nitrate, the simplest of the nitrates studied, we have the four frequencies 585, 869, 1290, and 1634. 1290, which is by far the strongest in methyl nitrate, appears in almost the same position in all the nitrates though the intensity gradually decreases. $\delta\nu$ 1634 appears equally prominent throughout except in the two propyl nitrates. The absence of this frequency in these two nitrates is inexplicable. $\delta\nu$ 869 is the strongest in all the spectra, and its value remains constant except in isopropyl nitrate, where it is considerably reduced in value. The greatest change is observed in $\delta\nu$ 585. This is very strong in the methyl and ethyl nitrates but is weak and diffuse in the iso-amyl nitrate. In the other nitrates its position is shifted considerably.

The NO_3 ionic frequencies.—The normal modes of vibration of the NO_3 ion have been calculated by several investigators following Dennison's method of treatment. The three oxygen atoms form an equilateral triangle with the nitrogen atom at the centre and in the plane of the triangle. Such a model gives rise to four frequencies,

two of which are single and the other two are each double. Of the two single frequencies, the one appears as a fundamental in the infra-red but is forbidden in the Raman effect, while the other is not so forbidden. On this dynamical basis we can explain the observed frequencies in the Raman effect of the nitrates where ionic frequencies can be expected. In inorganic nitrates, whose Raman spectra have been studied both in the crystalline form and in the form of solutions, three fundamental frequencies are obtained at 730, 1050, and 1360 respectively, and a fourth one at 1669. Of these 1050 is the strongest and this is, in fact, one of the single frequencies mentioned above, whose appearance in the Raman effect is not forbidden. 730 and 1360 are the double frequencies mentioned. The second of the single frequencies is forbidden to appear as a *fundamental* in the Raman effect, though it may well appear as an overtone and 1669 is the overtone frequency, the corresponding fundamental being 835.

Comparing these ionic frequencies in the inorganic nitrates with the frequencies observed in the organic nitrates, it is significant that none of the former is represented in the latter. This difference is probably due to the influence of the CH group on the NO_3 group in organic nitrates.

The question naturally suggests itself, if these ionic frequencies which are absent in the organic nitrates (pure liquids) may be expected in solutions of these nitrates, where the NO_3 group may be in an environment favourable to perform its own oscillations unhampered. Accordingly we studied two alcoholic solutions, viz., a 20 per cent solution of methyl nitrate in methyl alcohol and an equimolecular solution of iso-amyl nitrate in iso-amyl alcohol.

Methyl nitrate and methyl alcohol.—In the scattering by this solution only three lines appeared prominently. Their wave-lengths were 4600·5, 4575·4, and 4224·4 A.U., the corresponding wave-numbers being 21730, 21850, and 23665 cm.$^{-1}$ respectively. The first two were diffuse while the third was sharp. They were excited by λ 4046·6 or ν 24705 cm.$^{-1}$ of the mercury arc, and the frequency differences were 2975, 2855, and 1040. The first two shifts are evidently the CH frequencies, whose values are in methyl nitrate 2965 and in methyl alcohol 2940 and 2835. The strong shift 1040 is probably the characteristic nitrate ion frequency. It is significant that the strong shifts of methyl nitrate were absent to the exclusive appearance of this ionic frequency.

Amyl nitrate and amyl alcohol.—In this solution the Raman spectrum shows in addition to the 3·4 μ band, the shifts 1456 and 868. The 1040 shift is very faint.

It is difficult to say if the NO_3 group is present as free ion in the alcoholic solution; there is no other evidence to support this view. At least it is significant from the results mentioned above that the oscillations of the NO_3 group are less hampered by the CH group in alcoholic solutions than in the pure liquids. It may be mentioned in this connexion that the dielectric constant of methyl alcohol is very high, coming next to water with a value 35, while for amyl alcohol it is only 16. It will be interesting to study the influence of different solvents on the NO_3 oscillations in organic nitrates, and experiments in this direction are in progress.

The authors wish to express their thanks to Prof. M. Owen for his great intrest in this work. Our thanks are also due to the Chemistry Department of this College for the facilities afforded to us in the preparation of some of the nitrates studied.

College of Science, Nagpur.
May 1, 1932.

CXI. *Reaction Velocity in Reversible Systems* $Solid_1 \rightleftharpoons Solid_2 + Gas$. *By* B. Topley, *M.A.**

THE remarks which follow are restricted to systems in which the reactant and resultant solid phases do not form solid solutions. Dissociation of salt hydrates and ammoniates and of carbonates are reactions usually of this kind, and some of these have been studied kinetically, especially the reaction

$$CuSO_4.5H_2O \rightleftharpoons CuSO_4.H_2O + 4H_2O\ ^{(1)}.$$

The circumstances important in this particular example are certainly so in many other cases. The point discussed in this note is illustrated by reference to this reaction.

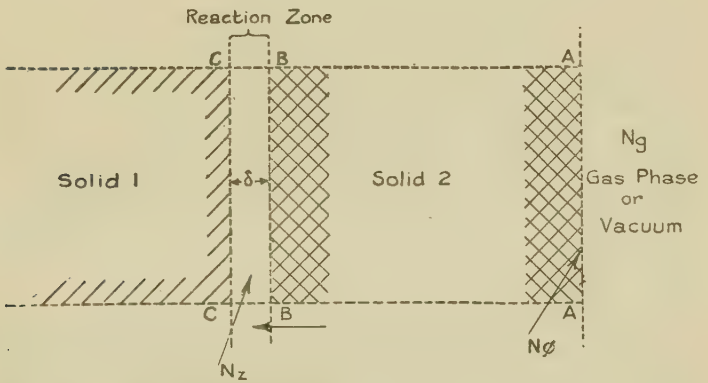
It is clear that the rate of reaction must be a function of the concentration of the gaseous product (referred to in general as G) in the atmosphere surrounding the solid

* Communicated by the Author.

system. The shape of the curve relating rate and concentration of G may be a complicated one when the whole range from zero concentration of G up to the equilibrium value is included, and it varies with the reaction [4].

Experimentally, the rate of reaction measured is the net rate of escape of molecules of G into the gas phase. This rate is ultimately dependent on the processes occurring in the interfacial zone between the two solid phases, which is the seat of the chemical reaction. The elementary acts of chemical change involve a thermal activation ; the physical meaning of this activation was discussed in a previous paper [5], and it was suggested, at any rate in the case of salt hydrates, that the activation is required to increase the energy

Fig. 1.



of a water molecule oscillating in the interface $S_1 : S_2$ until it surmounts a hill and falls into a valley on the potential energy diagram, the hill being the chemical bond tending to keep the water molecule attached to the hydrate lattice, the valley representing the state of adsorption on the opposite side of the reaction zone, *i.e.*, on to the lower hydrate or in general the $Solid_2$. The attractive force exerted by the $Solid_2$ plays an important part in lowering the height of this hill, so causing the autocatalytic phenomenon commonly observed in these reactions when steps are not taken to avoid it. In the case of reversible reactions it must also act in another way, which does not seem to have been noticed before ; the main object of this note is to draw attention to this point.

Fig. 1 represents the section of an element of volume of the reacting system, the reaction progressing in the direction

of the arrow. $Solid_2$ is produced in a porous form consisting of exceedingly small particles, more or less caked together forming a pseudomorph of the original crystal. The ease or otherwise of passage of G molecules through a given thickness of the layer of S_2 probably depends chiefly upon the proportion of unoccupied space contained in the pseudomorph, *i. e.*, upon the ratio of the molecular volumes of S_2 and S_1. The molecules of G find their way out by diffusion along irregular channels, probably by surface-diffusion on the surface of the particles of S_2. Except for occasional fissures or gross faults in the pseudomorph, the porous solid appears homogeneous to low power microscopic observation. It seems probable that the channels are so narrow that the diffusing molecules move in the attractive field of S_2 all the time. A molecule of G whilst it is inside the porous solid is subject to the adsorption potential of the "inner surface" of this solid. It is convenient to refer to G molecules moving inside the porous solid or in the reaction zone as "adsorbed," and molecules which are still attached to the lattice of S_1 but are vibrating into the reaction zone as "oscillator molecules." The final stage is the escape of molecules from the outer surface AA into the gas phase ; the magnitude of the adsorption potential ϕ is one factor controlling the concentration N_ϕ of adsorbed molecules in the outermost layers of the porous solid, and therefore controlling also the concentration N_z in the reaction zone.

One obvious result of the presence of S_2 is that to an increasing extent as the thickness increases, molecules of G are constrained to remain on the average longer in the reaction zone, where they influence the net rate of the reversible reaction. It has been pointed out in earlier papers [1] that this introduces a difficulty in arriving at the true rate of the forward component $S_1 \rightarrow S_2 + G$, which it is desired to determine. The method adopted to eliminate this disturbing effect (referred to as "impedance" by the solid product) was to extrapolate the reaction rate back to zero thickness of S_2. It was assumed that this procedure gave a corrected rate which measured the velocity of the dissociation reaction *under conditions such that the number of adsorbed molecules in the reaction zone would be zero.* In principle, however, this extrapolation does not give us the required rate, but another rate, the meaning of which is also quite definite. The reason is that, although the impedance effect arising simply from the resistance offered by S_2 to diffusion of G molecules may be (and is here assumed to be) successfully eliminated by the extrapolation, the part played by the

layer of S_2 in lowering the activation energy involves also the consequence that there must be a certain concentration of G molecules in the reaction zone, even in the limiting case of a thickness of S_2 so small that its impedance effect is negligible. It is possible to calculate the influence of this unavoidable concentration of G molecules upon the reaction velocity, from a knowledge of the sensitivity of the velocity to small concentrations of G in the gas phase; the problem is to determine the ratio of the two rates referred to above.

We define the reaction velocity constant as the number of molecules per unit area of reaction zone leaving the solid system in unit time.

Let R^0 = reaction velocity constant in a vacuum.

R' = reaction velocity constant in an atmosphere of G molecules at concentration N_g.

The superscripts ^{0} and $'$ are used to denote quantities referring to the reaction in vacuum or in the presence of a definite concentration of G molecules in the gas phase, respectively; when the superscript is omitted the symbol applies to both.

The model which we use here for the reacting system when the impedance is ignored is to regard the porous S_2 as equivalent to a space (bounded by AA and BB) possessing the property that any G molecule in it is at a potential energy level ϕ compared with the level zero in the gas phase. A fraction of this space is occupied by particles of S_2 itself; for the present purpose, therefore, the porous solid is considered to act as a fine-grained mixture of irregular shaped elements of volume, some having an adsorption potential ϕ for G molecules, the rest being inaccessible to G. In fig. 1 the concentrations N_ϕ and N_z denote number of molecules of G in unit volume of space not occupied by S_2. (In the case of the reaction

$$CuSO_4.5H_2O \rightleftharpoons CuSO_4.H_2O + 4H_2O$$

just over one-half of the total volume of the pseudomorph is accessible to adsorbed G molecules.) The reaction zone is then a narrow strip of this space adjoining the lattice S_1; the thickness δ of this strip is obviously of the order of magnitude of the range of molecular forces.

Suppose that there are n molecules of G oscillating in unit area in the reaction zone, still attached to the lattice S_1 but in a position to be thermally activated to the point of dissociation. For each G molecule which breaks away from

the lattice a definite small number $c-1$ follow immediately; e. g., c is 4 for the reaction

$$CuSO_4 . 5H_2O \rightarrow CuSO_4 . H_2O + 4H_2O \text{ (5)}.$$

Let l be the mean life of an oscillator molecule *in the complete absence of adsorbed molecules in the reaction zone.* The life is the time interval between the exposure of the molecule in the reaction zone by the advance of the reaction through the solid and its activation to the point of dissociation. This mean life is the fundamental quantity characteristic of the reaction, and a knowledge of l as a function of temperature is required for a test of any detailed hypothesis concerning the mechanism of the activation process.

The definition of K_1, the "true" reaction velocity constant of the dissociation reaction is

$$K_1 = n . cl^{-1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In practice, because of the impedance effect, rate measurements are most useful (from the point of view of determining K_1) when the thickness of S_2 is as small as possible, consistent with a sufficient extent of reaction for accurate measurement *. Therefore a geometrical factor, taking account of the change in interface area as the reaction proceeds, can be omitted for simplicity, and the area of the reaction zone taken as equal to the external area of the crystal. Under this condition the net rate of dissociation per unit area of reaction zone equals the net rate of transfer of molecules outwards from the reaction zone across unit area of any section parallel to the latter.

Applied to the outer surface of S_2 this gives

$$R' = N_{\phi}' \sqrt{\frac{kT}{2\pi m}} e^{-\frac{\phi}{kT}} - N_g \sqrt{\frac{kT}{2\pi m}}, \quad . \quad (2.1)$$

where $\frac{1}{2}kT$ = the mean translational energy per molecule in one degree of freedom;

m = the mass of a G molecule;

R', N_{ϕ}', and N_g have the meanings explained above.

Equation (2.1) is the ordinary kinetic theory expression for the transfer of molecules across the boundary AA.

* It is assumed that the experimental conditions (size of crystal, complete nucleation of the surface, and the question of the anisotropy of the crystal producing different values of K_1 in different directions) have been suitably chosen. *Cf.* reference (1).

assuming that N_ϕ' is small enough to justify neglect of the actual volume occupied by G molecules.

From (2.1) we get

$$N'_\phi = \frac{R' + N_g\sqrt{\frac{kT}{2\pi m}}}{\sqrt{\frac{kT}{2\pi m}}\, e^{-\frac{\phi}{kT}}} \quad . \quad . \quad . \quad . \quad (2.2)$$

and

$$N_\phi{}^0 = \frac{R^0}{\sqrt{\frac{kT}{2\pi m}}\, e^{-\frac{\phi}{kT}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.3)$$

Corresponding to the concentration N_ϕ' of molecules in the porous solid, there is a number $N_z'\delta$ per unit area of the reaction zone. If the concentration N_z' is sufficiently small, then, except for a negligibly small proportion, all the adsorbed molecules in the reaction zone can be regarded as separate, in the sense that the whole effect of the presence of one such molecule is exerted in a region which does not contain another adsorbed molecule. Within the restricted range over which this assumption holds, we shall have a linear relation connecting R' and N_z' :

$$R' = K_1 - BN_z', \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where B is a constant at constant temperature, and in principle may have either sign, but has so far always been found to be positive.

The impedance effect being eliminated, we have $N_z' = N_\phi'$ in (2.1), and combining this with (3) we have

$$R' = \frac{K_1 - Be^{\frac{\phi}{kT}} N_g}{1 + \frac{B}{\sqrt{\frac{kT}{2\pi m}}} e^{\frac{\phi}{kT}}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Within the range of validity of the assumptions made the reaction velocity constant varies linearly with the concentration of the gaseous product in the surrounding atmosphere. This leads to a simple formula for the true reaction velocity constant:—

From (4)

$$\frac{dR'}{dN_g} = \frac{-Be^{\frac{\phi}{kT}}}{1 + \frac{B}{\sqrt{\frac{kT}{2\pi m}}} e^{\frac{\phi}{kT}}}, \quad . \quad . \quad . \quad . \quad (5)$$

and combining this with (4),

$$K_1 = R' \left\{ \frac{\sqrt{\frac{kT}{2\pi m}}}{\sqrt{\frac{kT}{2\pi m}} + \frac{dR'}{dN_g}} \right\} + Be^{\frac{\phi}{kT}} N_g,$$

correspondingly, in the limit when N_g is kept at zero during the reaction,

$$K_1 = R^0 \left\{ \frac{\sqrt{\frac{kT}{2\pi m}}}{\sqrt{\frac{kT}{2\pi m}} + \left(\frac{dR'}{dN_g}\right)_{N_g \to 0}} \right\} . \quad . \quad . \quad (6)$$

or $K_1 = R^0 . Z,$

where Z is a numerical factor evaluated from the expression in brackets in (6). Thus Z can be determined from experimental measurement of two quantities, the rate measured in a vacuum and corrected to zero thickness of S_2, and the limiting slope of the tangent to the curve relating the rate to the concentration in the gas phase, when the latter approaches zero.

Application to the Reaction

$$CuSO_4 . 5H_2O \rightarrow CuSO_4 . H_2O + 4H_2O.$$

In a previous paper[1] measurements of the reaction velocity constant R^0 over a range of temperature were recorded, and summarised in the formula

$$\log_{10}(\text{reaction velocity constant}) = 12{\cdot}112 - \frac{3982}{T},$$

the units being mgm. H_2O per sq. cm. per minute. It was there stated that this represented the absolute rate of the decomposition reaction, unaffected by the reverse reaction or by water vapour "poisoning" of the interface. In the light of the discussion in the preceding section, this statement requires modification, since the constant which is really a measure of the rate of the reaction when taking place entirely uninfluenced by water molecules in the reaction zone is the K_1 of this paper, not the reaction velocity constant of the previous paper, which corresponds to R^0 in this paper.

The previous paper contained also the results of measurements of the effect upon the reaction rate of water vapour in

the atmosphere surrounding the crystal. These have now been supplemented by a new series of rate measurements at small water vapour concentrations, in an attempt to obtain the information required in order to make use of equation (6). The whole of the data available at one temperature are tabulated below.

The rates are all corrected for "self-cooling" of the crystals below the thermostat temperature. The experi-

Velocity Constants at 22·25° C. of the Reaction
$CuSO_4 . 5H_2O \rightarrow CuSO_4 . H_2O + 4H_2O$.

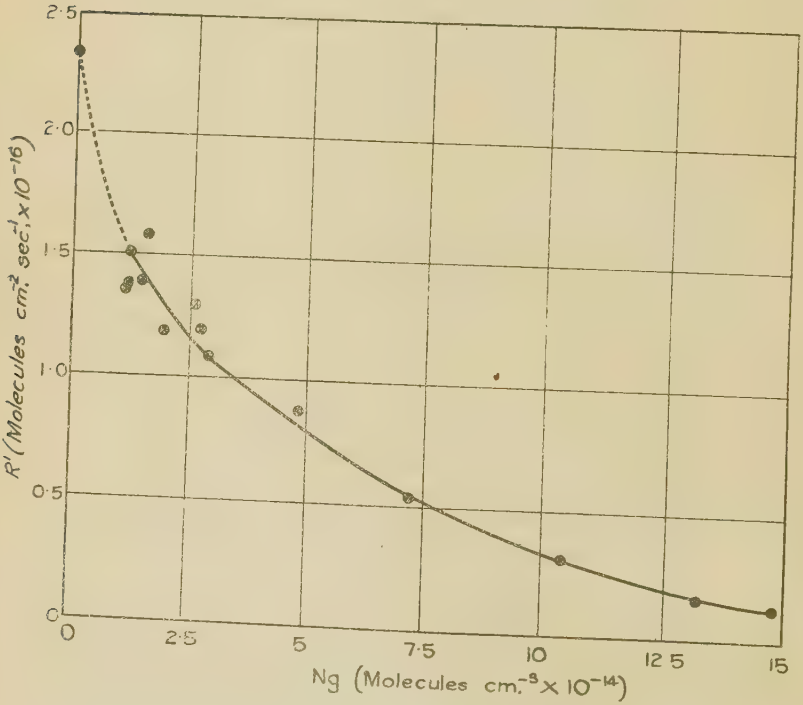
Method.	N_g (molecules cm.$^{-3}$ $\times 10^{-14}$).	R′ (molecules cm.^{2} sec.$^{-1}$ $\times 10^{-16}$).
Mean value	0	2·36
Flow	1·22	1·5
Flow	1·25	1·4
Static	1·45	1·4
Static	1·52	1·6
Flow	1·53	1·6
Flow	2·00	1·2
Flow	2·60	1·3
Flow	2·70	1·2
Static	2·96	1·1
Static	4·94	0·88
Static	7·24	0·54
Static	10·4	0·30
Static	13·2	0·14
Static	14·8	0·13

ments marked "Flow" were done in a stream of hydrogen at a few mm. Hg pressure, exactly as previously described; these are new experimental data. The data of the experiments done by the "Static" method are quoted from Table 5 of that paper, but are now converted into absolute units.

Fig. 2 shows these points and a curve drawn through them. The point on the axis of ordinates is more accurate than the other points, being the mean value from the formula given above, which summarizes all the experiments done in a vacuum with phosphorus pentoxide present in the reaction

vessel. Unfortunately, it was not possible to get more points in the important region near the vacuum point ($N_g=0$). The experimental difficulty which prevented the "Flow" method from being used for this purpose is that the reaction itself contributes a certain partial pressure of water vapour, which could only be reduced by using a smaller area of reaction zone, and thus at the expense of the accuracy of the rate measurement with the quartz spring micro-

Fig. 2.



balance. The "Static" method fails at very low pressures because pressure equilibrium is not established rapidly enough throughout the apparatus[1].

The experimental results do no more than indicate that the curve may become linear in the immediate neighbourhood of the "vacuum" point. It is not a theoretical necessity that it should do so, because the condition for the linear relationship (3) might fail even with $N_g=0$ (if, for example, ϕ is large and R^0 not sufficiently small). But

since there are at present no other data of this kind available, it is interesting to calculate out the value of the factor Z, making the assumption that equation (3) is justified, as a working hypothesis.

The initial tangent to the curve drawn so that it runs up to the well-established point on the axis of ordinates without any violent curvature is -97 cm. sec.$^{-1}$. Subject to the proviso already emphasized, the value of $\left(\frac{dR'}{dN_g}\right)_{N_g \to 0}$ can be taken as lying between the limits -97 ± 50 per cent. The corresponding value of Z in equation (6.1) is $1{\cdot}007 \pm {\cdot}0035$.

Thus the result of taking into account the point discussed in this paper is to indicate that the "true" value of the reaction velocity constant for the dissociation reaction

$$CuSO_4 . H_2O \rightarrow CuSO_4 . H_2O + 4H_2O$$

may be (at least) about 1 per cent. higher than the experimental velocity constant (R^0) at 22·25° C.

The factor Z probably has a similar small value over the temperature range 0° to 43°, because, although the actual reaction rate, and therefore also the concentration of water molecules in the reaction zone, decreases rapidly as the temperature is lowered, the sensitivity to water vapour increases at the same time. An indirect argument supporting this conclusion is that the measured reaction velocity constant (R^0) gives a straight line plot of log R^0 against 1/T between 0° and 43°, the velocity increasing 100-fold in this range. If the reaction rate were affected by a large factor Z over the whole or part of this range, only an improbable coincidence could explain the observed temperature influence.

Summary.

The reaction velocity constant for reversible reactions involving two solid phases, obtained by extrapolation of rate measurements back to zero thickness of the solid product, requires further correction to determine the mean life of a molecule in the reaction zone before breaking away from the lattice of the reactant solid.

When the reaction velocity varies linearly with the concentration of gaseous product surrounding the solid, the correction required is multiplication by a factor involving the rate of change of the reaction velocity with the concentration of gaseous product.

New measurements of the influence of small concentrations of water vapour on the velocity of the reaction

$$CuSO_4 . 5H_2O \rightarrow CuSO_4 . H_2O + 4H_2O$$

are recorded ; the available data indicate that the correction is of the order of 1 per cent. for this reaction at 22·25° C.

References.

(1) Smith and Topley, Proc. Roy. Soc. A, cxxxiv. p. 224 (1931).
(2) Garner and Tanner, J. Chem. Soc. cxxv. p. 47 (1930).
(3) Hume and Colvin, Proc. Roy. Soc. A, cxxxii. p. 548 (1931).
(4) Topley and Smith, 'Nature,' Aug. 1931.
(5) Topley, Proc. Roy. Soc. A, cxxxvi. p. 413 (1932).

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CXII. *Some Aspects of the Geometry of the Jamin Refractometer.* *By* S. E. Green, *A.R.C.S., D.I.C., B.Sc., Lecturer in Physics, Imperial College of Science and Technology* *.

Introduction.

FOR the determination of the refractive index of a gas by means of a Jamin refractometer, the use of white light possesses considerable advantages. While the result obtained can be no more than an average value corresponding to the visible spectrum as a whole, this is often not a serious objection, since the dispersion produced by gases is small. The necessity for counting interference fringes is obviated, and, in addition, when employing a gas of known refractive index as a standard of comparison, the instrument can readily be adjusted by means of the compensator to bring to equality the optical paths traversed by the interfering rays.

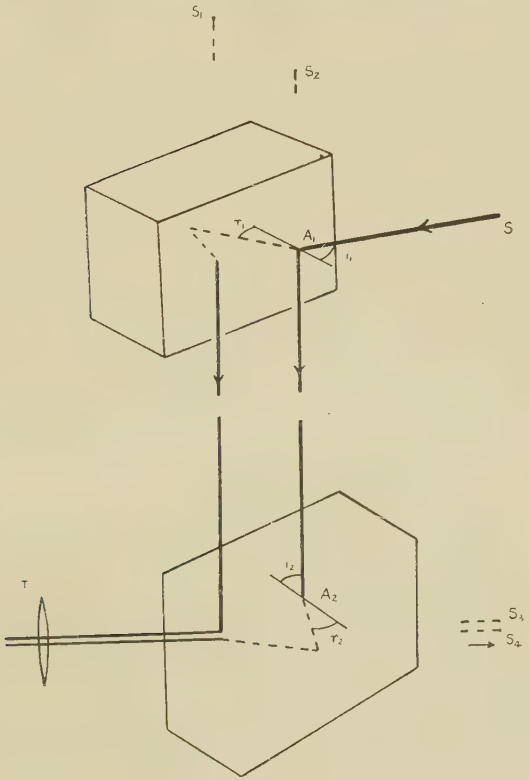
It is, however, of theoretical interest to ascertain the circumstances in which, in the absence of the compensator, the refractometer plates alone will give equality of optical path, that is, to determine how the plates must be orientated in order that white-light bands will be observable in the telescope.

The system of straight bands seen on using an extended source of light may be regarded as arising from the presence

* Communicated by the Author.

in the second plate of a pair of images of equal intensity, such as S_3 and S_4 (fig. 1), corresponding to each point of the source *. If the plates are parallel-sided, only parallel rays from these images give rise to the fringes, which are thus always formed in the focal plane of the telescope.

Fig. 1.



The following *ad hoc* method of treatment, while not of such general application as that of considering a hypothetical thin film between the plates, is of advantage, in the case of the Jamin refractometer, as illustrating directly the three dimensional geometry of the instrument as it stands.

The resultant difference between the paths traversed by the interfering rays (derived from a primary ray such as

* See Preston, 'Theory of Light.'

SA_1, fig. 1), on being brought to a focus by the telescope lens T, is given by the expression

$$2\mu_1 t_1 \cos r_1 - 2\mu_2 t_2 \cos r_2$$

in which μ_1, t_1, and r_1 represent the refractive index, thickness, and angle of refraction respectively pertaining to the first plate, and μ_2, t_2, and r_2 the corresponding quantities relating to the second. The separate terms in the expression give the path difference imposed by the respective plates. Hence if the latter are cut from the same block of glass, with the result that the optical constants of the plates are equal, it follows that the path difference will be zero for any incident ray such as SA_1 when the plates are so adjusted that $i_1 = i_2$. Under these circumstances a beam of incident rays parallel to SA_1 will give rise in the focal plane of the telescope to a point on the central fringe of the white-light system. If this point of interference coincides with the intersection of the cross-wires the rays producing it will enter the telescope parallel to the optic axis. The assumption is made, for convenience, that the optic axis of the telescope passes through the intersection of the cross-wires.

It is therefore required to determine what must be the relative orientations of the plates in order that for pairs of rays interfering in the telescope after having entered parallel to its optic axis, the angles of incidence on the glass plates (as at A_1 and A_2, fig. 1) are equal.

For simplicity the axes of the gas tubes are taken to be coplanar with, and at right angles to, the axis of the telescope. This common plane is taken as the standard plane of reference, planes parallel to it being called for convenience horizontal. The presence of the gas tubes may be disregarded, provided that the four end plates are of equal thickness and are perpendicular to the axes of the tubes, and, further, that the tubes contain gases of equal refractive index, as, for example, when both are open to the atmosphere. The question of the plane of reference is further considered in Appendix II., p. 1100.

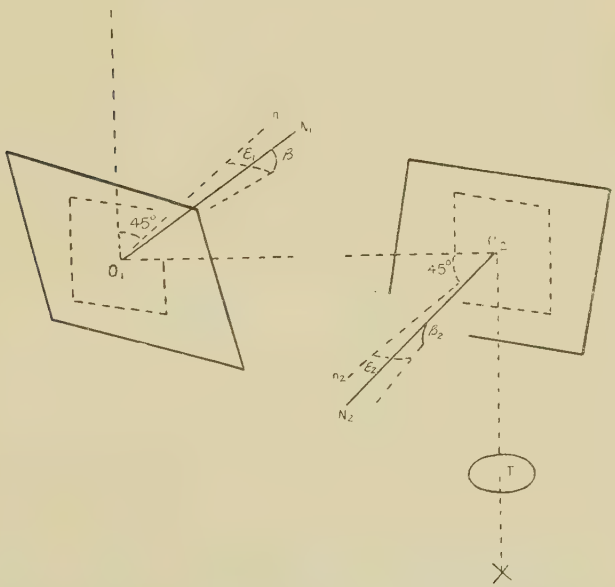
The zero orientations of the plates are taken as vertical, the normals in the plane of reference, *e.g.*, O_1n_1 and O_2n_2 (fig. 2) being inclined at 135° and 45° to the axis of the telescope in the case of the first and second plates respectively. In any displaced position the orientation of the first plate may be regarded as derived by rotation from the zero position through an angle ϵ_1 in the horizontal direction and an angle β_1 in the vertical. Corresponding angles ϵ_2, β_2 apply to the second plate. Thus in the displaced positions

any normals to the first and second plates are parallel to the lines O_1N_1, O_2N_2 respectively. In fig. 2 all discontinuous lines, with the exception of those indicating the zero orientations of the plates, lie in the standard plane.

Deviation at the First Plate.

In fig. 3 a typical ray SA_1 is shown incident upon the first plate at A_1. A_1x and A_1y are straight lines lying in the

Fig. 2.



horizontal plane through A_1 and at right angles to each other, A_1x being parallel to the axis of the telescope. Angles α and δ, the angles of reference of the incident ray, denote respectively the inclination of SA_1 to the horizontal plane and the angular displacement in the horizontal direction from A_1x. Corresponding angles α_1 and δ_1 pertain to the reflected ray A_1A_0. A_1N_1 is the normal to the plate, while in the zero orientation of the plate all normals are parallel to A_1n_1, which bisects the right angle xA_1y. In the diagram all horizontal lines are dotted.

Then it follows that (as shown in Appendix I., p. 1100),

$$\alpha_1 = \alpha - \sqrt{2}\beta_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

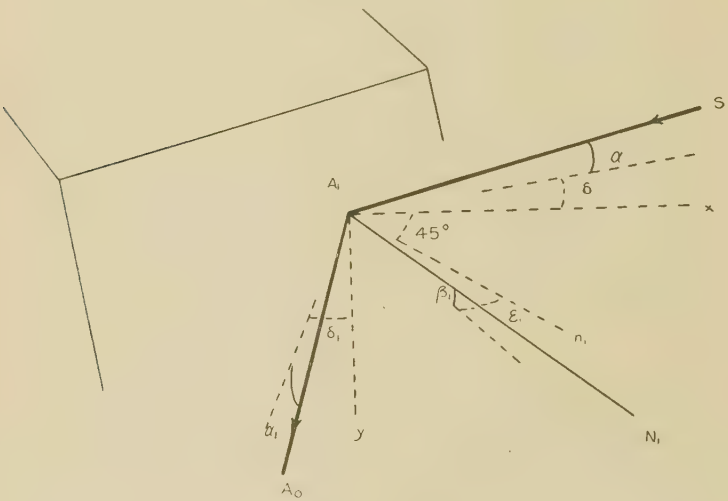
and

$$\delta_1 = \delta + 2\epsilon_1 + \beta_1^2 - \sqrt{2}\alpha\beta_1, \quad . \quad . \quad . \quad . \quad (2)$$

provided all the angles involved are small, a condition which is satisfied in the practical use of the refractometer.

These relations, although giving δ_1 to the second order, but α_1 only to the first, are sufficient for the present purpose, since it is finally required to derive an equation connecting ϵ_1, ϵ_2, β_1, and β_2, the angles which express the orientations of

Fig. 3.



the plates, and such an equation will be adequate which involves not more than squares or products of these angles. That the above relations are, under these conditions, sufficient, will be obvious from consideration of (11), p. 1096.

Deviation at the Second Plate.

Fig. 4 shows the ray A_0A_2, which after leaving the first plate at A_1 is incident upon the second plate at A_2. All lines lying in the horizontal plane through A_2 are drawn discontinuously. It is clear that with the system of measurement adopted the angles of reference of any ray when leaving the first plate and when incident upon the second are the same.

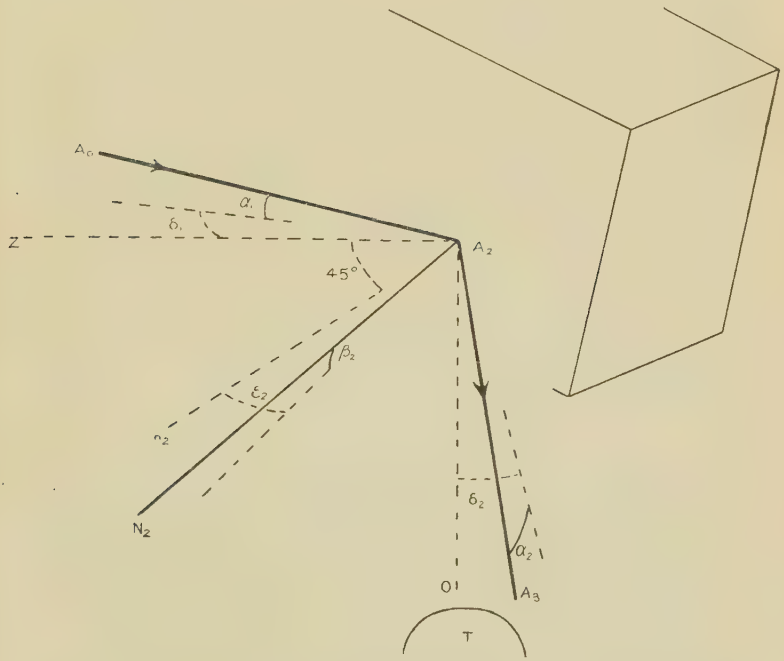
Thus α_1, δ_1 are the angles of reference of the incident ray A_0A_2 (fig. 4). Then, by analogy with relations (1) and (2), the angles of reference α_2, δ_2 of the interfering rays after leaving the second plate are given by

$$\alpha_2 = \alpha_1 - \sqrt{2}\beta_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and

$$\delta_2 = \delta_1 + 2\epsilon_2 + \beta_2^2 - \sqrt{2}\alpha_1\beta_2. \quad . \quad . \quad . \quad . \quad (4)$$

Fig. 4.



Since only rays which fall upon the telescope lens in the direction parallel to the optic axis are considered, and for such rays $\alpha_2 = \delta_2 = 0$, then

$$\alpha_1 = \sqrt{2}\beta_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$\delta_1 = \beta_2^2 - 2\epsilon_2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

So that from equations (1) and (2),

$$\alpha = \sqrt{2}(\beta_1 + \beta_2), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\delta = (\beta_1 + \beta_2)^2 - 2(\epsilon_1 + \epsilon_2). \quad . \quad . \quad . \quad . \quad (8)$$

These relations give the direction of incident rays such as SA_1, for which the component rays interfere on the cross-wire of the telescope.

Deduction of the required Relation.

In order that this point of interference shall in addition lie on the central fringe of the white-light system, the further condition has to be satisfied that the angle of incidence of each original ray upon the first plate shall be equal to the angle of incidence of the interfering components of that ray upon the second plate. By reference to figs. 3 and 4 respectively

$$\cos SA_1N_1 = \sin\alpha\sin\beta_1 + \cos\alpha\cos\beta_1\cos(45+\delta+\epsilon_1), \quad (9)$$

and

$$\cos A_0A_2N_2 = \sin\alpha_1\sin\beta_2 + \cos\alpha_1\cos\beta_2\cos(45+\delta_1+\epsilon_2). \quad (10)$$

From the right-hand sides of these relations, the equation representing equality of angle of incidence becomes

$$\sin\alpha\sin\beta_1 + \cos\alpha\cos\beta_1\,[\cos(\delta+\epsilon_1) - \sin(\delta+\epsilon_1)]/\sqrt{2}$$
$$= \sin\alpha_1\sin\beta_2 + \cos\alpha_1\cos\beta_2[\cos(\delta_1+\epsilon_2) - \sin(\delta_1+\epsilon_2)]/\sqrt{2},$$

which gives, by the retention of no higher terms than squares or products of angles,

$$2\sqrt{2}(\alpha\beta_1 - \alpha_1\beta_2) = (\alpha^2+\beta_1^2) - (\alpha_1^2+\beta_2^2)$$
$$+ (\delta+\epsilon_1)^2 - (\delta_1+\epsilon_2)^2 + 2(\delta+\epsilon_1) - 2(\delta_1+\epsilon_2). \quad (11)$$

This equation relates the orientations of the plates to the directions of any interfering rays for which the final path difference is zero, *i. e.*, those interfering rays which come to a focus at a point on the central white fringe. For any such point to lie on the intersection of the cross-wires in the telescope, relations (7), (8), (5), and (6) must be satisfied in addition. Eliminating α, δ, α_1, δ_1 in this way from (11), the required connexion between the orientations of the plates for zero path difference at the cross-wire reduces, as far as second-order terms are concerned, to

$$(\beta_1+\beta_2)(\beta_1+3\beta_2) = 2(\epsilon_1+\epsilon_2). \quad . \quad . \quad . \quad (12)$$

As a check on this result, the sums of the angles of incidence and reflexion at the two plates may be equated, giving

$$\cos SA_1A_0 = \cos A_0A_2A_3 \qquad \text{(figs. 3 and 4)}$$

i. e., putting $\alpha_2 = \delta_2 = 0$

$$-\sin\alpha\sin\alpha_1 + \cos\alpha\cos\alpha_1\cos(90+\delta+\delta_1) = \cos\alpha_1\cos(90+\delta_1).$$

Expanding as far as squares or products of the angles, this reduces to $-\alpha\alpha_1 = \delta$, which by substitution from (5), (7), and (8), in terms of angles giving the orientations of the plates, gives (12) above.

This, then, is the required relation satisfied by the orientations of the plates (for small displacements from the zero positions) whenever the central fringe of the white-light system lies on the intersection of the cross-wires in the telescope.

Conformity to general Considerations.

The derived relation conforms to two conditions imposed by general considerations. The first is that the path difference of the interfering rays must always be zero for perfect parallelism of the plates. Under these circumstances, given exactly similar and parallel-sided plates, images S_3 and S_4 (fig. 1) of each point of the source are brought into coincidence. Further, when the plates are parallel the angle of refraction at the first plate is equal to that at the second, whatever the angle or direction of incidence upon the first plate may be. Hence no interference pattern is formed, the path difference between interfering rays being zero at every point of the focal plane of the telescope. It is seen that relation (12) is satisfied whenever $(\beta_1+\beta_2)$ and $(\epsilon_1+\epsilon_2)$ vanish together, *i.e.*, in all cases in which the plates are parallel.

Further, under these circumstances, the rays which are brought to a focus on the cross-wire must be derived from primary rays which are incident upon the first plate in directions parallel to the axis of the telescope. If the plates are parallel it is seen that $\alpha=\delta=0$, by relations (7) and (8).

The second condition, to which on general grounds relation (12) must conform, is that if white-light fringes appear in the telescope for any given orientations of the plates, they must by symmetry reappear if the vertical displacements (β_1 and β_2) of the plates are reversed together, the horizontal displacements remaining unaltered. Clearly this condition is satisfied. The direction of the incident light giving zero path difference at the cross-wire will be different in the two cases, being simply reversed in the vertical direction. Since by (7) $\alpha = \sqrt{2}(\beta_1+\beta_2)$, and (8) and (12) in addition give $\delta=-\sqrt{2}\beta_2\alpha$ the reversal of β_1 and β_2 changes the sign of α only.

It is evident that the central interference band cannot be made to appear on the cross-wire for all directions of inci-

dence upon the first plate. The possible directions are confined to those for which $\delta = -\sqrt{2}\beta_2\alpha$, and thus the possible deviations of the incident light from parallelism in the horizontal direction with the axis of the telescope are much smaller than the corresponding inclinations to the plane of reference, the former being of the second order.

If the angles in relation (12) are expressed in degrees the equation becomes

$$(\beta_1+\beta_2)(\beta_1+3\beta_2) = (\epsilon_1+\epsilon_2)360/\pi,$$

i. e.,

$$(\epsilon_1+\epsilon_2) = (\beta_1+\beta_2)(\beta_1+3\beta_2)/115.$$

If the vertical angular displacements β_1, β_2 of the plates be measured in degrees while the sum of the corresponding horizontal displacements ϵ_1, ϵ_2, being of necessity much smaller than the vertical angles, is measured in minutes of arc, then

$$(\epsilon_1+\epsilon_2) = 0{\cdot}522(\beta_1+\beta_2)(\beta_1+3\beta_2).$$

Typical figures are given in the following table :—

Values of $(\epsilon_1+\epsilon_2)$ in Minutes of Arc.

β_2 degrees.	β_1 degrees. −2·5.	−2.	−1.	0.	1.	2.	2·5.
−2	20·0	16·7	11·0	6·26	2·61	0·00	−0·92
−1	10·1	7·83	4·18	1·57	0·00	−0·52	−0·39
0	3·26	2·09	0·52	0·00	0·52	2·09	3·26
1	−0·39	−0·52	0·00	1·57	4·18	7·83	10·1
2	−0·92	0·00	2·61	6·26	11·0	16·7	20 0

These figures are plotted in the set of curves for constant values of β_1 given in fig. 5. The curves for positive values of β_1 are shown dotted. For a given value of β_1, $(\epsilon_1+\epsilon_2)$ attains its minimum when $\beta_2 = -2\beta_1/3$ The sum of the horizontal displacements of the plates $(\epsilon_1+\epsilon_2)$ is negative only when the vertical displacements have together numerically large values of opposite sign. By putting ϵ_1 equal to zero the curves give the variation in orientation of the second plate for different fixed values of the vertical displacement of the first.

Appendix I.

Derivation of Relations (1) *and* (2).

Referring to fig. 3 the laws of reflexion are embodied in the equations

$$\text{angle } SA_1N_1 = \text{angle } N_1A_1A_0 = 1/2 \text{ angle } SA_1A_0. \quad (13)$$

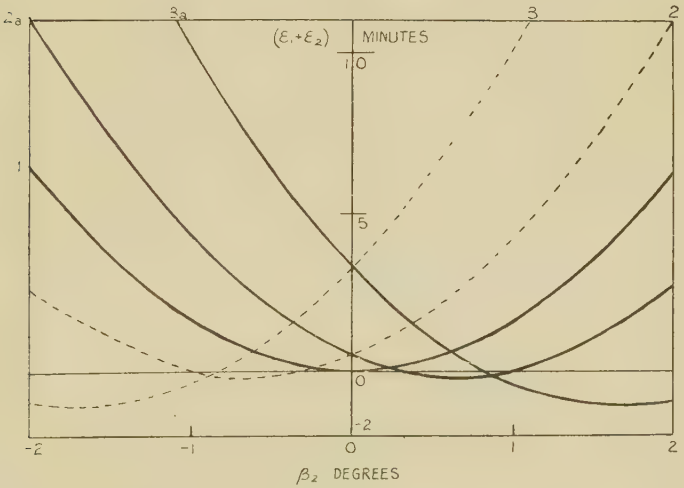
By a well-known theorem in spherical trigonometry

$$\cos SA_1N_1 = \sin\alpha \sin\beta_1 + \cos\alpha \cos\beta_1 \cos(45+\delta+\epsilon_1) \quad (14)$$

and

$$\cos NA_1A_0 = -\sin\alpha_1 \sin\beta_1 + \cos\alpha_1 \cos\beta_1 \cos(45+\delta_1-\epsilon_1). \quad (15)$$

Fig. 5.



For curve 1. $\beta_1 = 0$.

" 2. / 2a. } $\beta_1 = \pm 1°$ resp.

" 3. / 3a. } $\beta_1 = \pm 2{\cdot}5°$ resp.

Expansion of the right-hand sides of (14) and (15) as far as terms involving squares and products of the angles, gives respectively,

$$\alpha\beta_1 + \frac{1}{\sqrt{2}}\left[1 - \frac{\alpha^2}{2} - \frac{\beta_1^2}{2} - (\delta+\epsilon_1) - \frac{(\delta+\epsilon_1)^2}{2}\right]$$

and

$$-\alpha_1\beta_1 + \frac{1}{\sqrt{2}}\left[1 - \frac{\alpha_1^2}{2} - \frac{\beta_1^2}{2} - (\delta_1-\epsilon_1) - \frac{(\delta_1-\epsilon_1)^2}{2}\right].$$

The first of relations (13) above then reduces to

$$2\sqrt{2}(\alpha\beta_1+\alpha_1\beta_1)+\alpha_1{}^2-\alpha^2 = (\delta-\delta_1+2\epsilon_1)(2+\delta+\delta_1). \quad (16)$$

Writing $\delta_1-\delta-2\epsilon_1 = x$, it follows that x is a function of square and higher terms, so that equation (16) becomes, on rejecting the third-order quantity $x(\delta+\delta_1)$,

$$(\alpha+\alpha_1)(2\sqrt{2}\beta_1+\alpha_1-\alpha) = -2x. \quad . \quad . \quad (17)$$

The condition that angle SA_1N_1 is half angle SA_1A_0 gives the relation

$$2\cos^2 SA_1N_1 = 1+\cos SA_1A_0. \quad . \quad . \quad (18)$$

The left-hand side becomes, by the retention of not more than the second order,

$$2\sqrt{2}\alpha\beta_1+1-\alpha^2-\beta_1{}^2-2(\delta+\epsilon_1),$$

and the right-hand side

$$1-\sin\alpha\sin\alpha_1+\cos\alpha\cos\alpha_1\cos(90+\delta+\delta_1),$$

or $1-\alpha\alpha_1-\delta-\delta_1$ neglecting terms beyond the second order.

Relation (18) thus reduces to

$$\alpha^2+\beta_1{}^2-\alpha\alpha_1-2\sqrt{2}\alpha\beta_1 = \delta_1-\delta-2\epsilon_1 = x. \quad . \quad (19)$$

By elimination of x from (17) and (19), which must be satisfied together, it follows that

$$(\alpha_1-\alpha+\sqrt{2}\beta_1)^2 = 0,$$

i. e.,
$$\alpha_1 = \alpha-\sqrt{2}\beta_1. \quad . \quad . \quad (1)$$

Hence from (19),

$$x = \beta_1{}^2-\sqrt{2}\alpha\beta_1,$$

or
$$\delta_1 = \delta+2\epsilon_1+\beta_1{}^2-\sqrt{2}\alpha\beta_1. \quad . \quad . \quad . \quad (2)$$

Equations (1) and (2) are the fundamental relations employed in the consideration of the deviation of rays by the plates.

Appendix II.

Independence of the Derived Relation of the particular Plane of Reference adopted.

While the standard plane has for practical symmetry been chosen as passing through the axes of the gas tubes, the only theoretical limitation imposed on the choice of such a plane is that it should pass approximately through the centres of the refractometer plates, thus ensuring that the measured displacements are always small. Thus if any new plane of reference be adopted, containing the axis of the telescope,

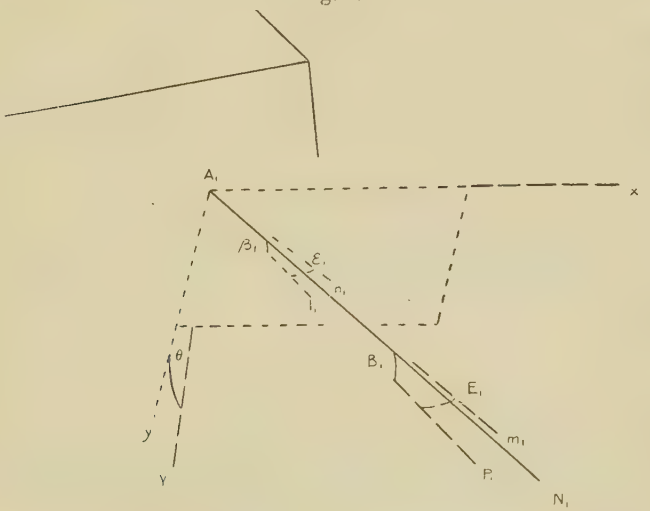
but slightly inclined to the original standard plane, and the orientations of the two plates are now defined by (E_1B_1) and (E_2B_2) respectively, then it should follow that

$$(B_1+B_2)(B_1+3B_2) = 2(E_1+E_2) \quad \ldots \quad (12a)$$

whenever the central fringe appears on the cross-wire.

Fig. 6, referring to the first plate, shows, passing through the point of incidence A_1, the plane xA_1y parallel to the original standard plane, and xA_1Y parallel to the new plane of reference, the two being inclined at a small angle θ. Lines in the second plane are drawn with dashes, A_1m_1

Fig. 6.



bisecting the right angle xA_1Y. Then A_1N_1 being normal to the plate,

$$\cos xA_1N_1 = \cos(45+E_1)\cos B_1 = \cos(45+\epsilon_1)\cos\beta_1$$

and

$$\cos N_1A_1Y = \cos(45-E_1)\cos B_1 = -\sin\theta\sin\beta_1 + \cos\theta\cos\beta_1\cos(45-\epsilon_1).$$

These equations give respectively, to the second order,

$$1-E_1-\frac{(E_1^2+B_1^2)}{2} = 1-\epsilon_1-\frac{(\epsilon_1^2+\beta_1^2)}{2} \quad \ldots \quad (20)$$

and

$$1+E_1-\frac{(E_1^2+B_1^2)}{2} = -\sqrt{2}\theta\beta_1+1-\frac{(\theta^2+\beta_1^2)}{2}+\epsilon_1-\frac{\epsilon_1^2}{2}.$$

Hence, by subtraction,

$$2E_1 = 2\epsilon_1 - \sqrt{2}\theta\beta_1 - \frac{\theta^2}{2}. \quad . \quad . \quad . \quad . \quad . \quad (21)$$

From relation (20),

$$\beta_1^2 - B_1^2 = (2 + \epsilon_1 + E_1)(E_1 - \epsilon_1) = 2(E_1 - \epsilon_1)$$

as far as the second order is concerned.

Hence, from (21),

$$\beta_1^2 = B_1^2 - \sqrt{2}\theta\beta_1 - \frac{\theta^2}{2},$$

i.e.,
$$\beta_1 = B_1 - \theta/\sqrt{2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

and thus by (21)
$$\epsilon_1 = E_1 + \theta B_1/\sqrt{2} - \frac{\theta^2}{4}. \quad . \quad . \quad . \quad . \quad (23)$$

Analogous treatment in the case of the second plate shows the new angles of reference E_2, B_2 to be given by the relations

$$\beta_2 = B_2 + \theta/\sqrt{2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

and
$$\epsilon_2 = E_2 + \theta B_2/\sqrt{2} + \theta^2/4. \quad . \quad . \quad . \quad (25)$$

From (22), (23), (24), and (25) it follows that equation (12*a*) above holds whenever the derived relation (12) is satisfied.

CXIII. *On Reactions in Solids: A Comparison of the Methods of Deriving the Energy of Activation.* *By* R. S. Bradley, *M.A.*, J. Colvin, *Ph.D.*, *and* J. Hume, *B.Sc.**

IT has been shown by the authors[1] that the whole of the decomposition time curve for the dehydration of calcium carbonate hexahydrate could be accounted for, if, in addition to the rate of advance of the interface between hydrated and anhydrous salt, an allowance were made for a finite rate of nucleation. Crystals were assumed to nucleate according to a probability law, and once a crystal had been nucleated at a point on the surface the reaction was supposed to spread instantaneously over the whole surface and then to propagate inwards. Flat plates were found the best form of crystal to use, and for these it happens that the theory is readily soluble. The velocity of the interface and the nucleation

* Communicated by the Authors.

constant could be calculated in a straightforward manner and the energies of activation could be found from measurements at different temperatures.

Calculation of Tangent of Maximum Slope for Flat Plates.

For flat plates

$$\alpha = \frac{2u}{\theta}\left(t + \frac{e^{-kt}-1}{k}\right),$$

where α is the fractional decomposition, u the rate of propagation, k the nucleation constant, θ the thickness of the plates, t the time from the start of the reaction. This expression holds up to $t = \frac{\theta}{2u}$. After this point

$$\alpha = \frac{2u}{\theta}\left[\frac{\theta}{2u} + \frac{e^{-kt}}{k}\left(1 - e^{\frac{k\theta}{2u}}\right)\right].$$

These two expressions have the same value at $t = \frac{\theta}{2u}$ and the same value for $\frac{d\alpha}{dt}$. They pass continuously into one another at this point and it is immaterial which is used, provided the point $t = \frac{\theta}{2u}$ is chosen. This is, in fact, the point of maximum slope, and here the curve is approximately linear. It might be thought that by measuring this linear slope for runs at different temperatures, a true energy of activation could be calculated. This is not the case, as is readily shown.

$$\frac{d\alpha}{dt} = \frac{2u}{\theta}(1 - e^{-kt});$$

$$\therefore \quad \text{maximum rate} = \frac{2u}{\theta}\left(1 - e^{\frac{-k\theta}{2u}}\right).$$

$$\log(\text{maximum rate}) = \log\frac{2u}{\theta} + \log\left(1 - e^{\frac{-k\theta}{2u}}\right).$$

$$\frac{d\log(\text{maximum rate})}{dT} = \frac{1}{u}\cdot\frac{du}{dT} + \frac{\frac{\theta}{2u}e^{\frac{-k\theta}{2u}}\cdot\frac{dk}{dT} - \frac{k\theta}{2u^2}e^{\frac{-k\theta}{2u}}\frac{du}{dT}}{1 - e^{\frac{-k\theta}{2u}}}.$$

$$= \frac{d\log u}{dT} + \frac{\frac{k\theta}{2u}e^{\frac{-k\theta}{2u}}\frac{d\log k}{dT} - \frac{k\theta}{2u}e^{\frac{-k\theta}{2u}}\frac{d.\log u}{dT}}{1-e^{\frac{-k\theta}{2u}}}$$

$$= \frac{E_u}{RT^2} - \frac{k\theta}{2u}\frac{e^{\frac{-k\theta}{2u}}}{1-e^{\frac{-k\theta}{2u}}}\left(\frac{E_u}{RT^2} - \frac{E_k}{RT^2}\right).$$

Thus an energy of activation for the interfacial motion which is less than the true one E_u (since $E_u > E_k$) would be obtained by measuring the tangents of maximum slope at different temperatures.

Topley and Hume [2] adopted a method for measuring the energy of activation for the motion of the interface which was designed to eliminate any differences in interfacial area when reaction rates at two different temperatures were compared by using "split runs" in which the reaction vessel was changed suddenly from one temperature to another. It is clear that if the tangents can be measured immediately before and immediately after the change a true energy of activation for the velocity of propagation may be obtained, since the measurements at different temperatures are then made on the crystals under comparable conditions.

In practice, however, no such instantaneous measurement is possible, since the dilatometer used takes time to attain a uniform temperature. Since nucleation must be considered if the whole decomposition-time curve is to be accounted for, it may be that by the time useful measurements can be made after changing to the new temperature, the altered nucleation rate is important. This can be settled by following the split run by the theory, allowance being made for nucleation. Two cases will be considered, in which the crystals are flat plates and spheres.

Calculation of a Split Run for Flat Plates.

$$\alpha_1 = \frac{2u_1}{\theta}\left(t_1 + \frac{e^{-k_1t_1}-1}{k_1}\right),$$

where the subscript 1 refers to temperature T_1. Now at time t_1 let the temperature become T_2. At t_1, the number of particles nucleated is $n_0(1-e^{-k_1t_1})$, the number unaffected $n_0e^{-k_1t_1}$, where n_0 is the total number of particles present.

At time t_3, t_2 minutes after t_1 $(t_3 = t_1 + t_2)$, the fractional decomposition is given by

$$\alpha_2 = \alpha_1 + \frac{n_0(1-e^{-k_1 t_1})2u_2 t_2 \mathrm{B}}{n_0 \mathrm{B}\theta} + e^{-k_1 t_1}\frac{2u_2}{\theta}\left(t_2 + \frac{e^{-k_2 t_2}-1}{k_2}\right),$$

where B is the mean area of the upper or lower surface of a crystal;

$$\therefore \quad \left(\frac{d\alpha_2}{dt_2}\right)_{\mathrm{T}=\mathrm{T}_2}^{t=t_1+t_2} = \frac{2u_2}{\theta}(1-e^{-k_1 t_1}) + \frac{2u_2}{\theta}e^{-k_1 t_1}(1-e^{-k_2 t_2}).$$

When $t_2 = 0$ we have the instantaneous tangent

$$\frac{2u_2}{\theta}(1-e^{-k_1 t_1}),$$

and hence the ratio of the instantaneous tangents is the ratio of the u's, so that the method of splitting the run would give a true energy of activation E_u if instantaneous tangents could be measured.

To investigate the error obtained in actual practice, let t_2 take the value 10 minutes. The error is $\frac{2u_2}{\theta}.e^{-k_1 t_1}(1-e^{-k_2 t_2})$, the percentage error $e^{-k_1 t_1}\left(\frac{1-e^{-k_2 t_2}}{1-e^{-k_1 t_1}}\right).100$.

Take $t_1 = 300$ minutes—approaching the linear portion of the curve. Taking the values from the previous paper[1], we have

$\mathrm{T}_1 = 7{\cdot}07°$, $k_1 = 9{\cdot}7 \times 10^{-3}$ min^{-1}, $t_2 = 10$ mins.

$\mathrm{T}_2 = 10{\cdot}07°$, $k_2 = 17{\cdot}1 \times 10^{-3}$ min^{-1}, $t_1 = 300$ mins.

This gives a percentage error of 0·9 approximately. When t_2 is 30 minutes, the error rises to 2·3 per cent., so that after the sudden change in temperature the theoretical curve is practically straight. The method of splitting the run is therefore sound not only for the ideal case of instantaneous tangents but also for the practically realizable case, where finite lengths of the curve must be observed before tangents can be measured. Owing, however, to the difficulty of measuring tangents graphically, especially after an abrupt kink in the curve, the method of analysis in terms of nucleation is to be preferred.

In the case of a split run with flat plates all the nucleated crystals have the same interfacial area. This is not so when spherical crystals are considered, and it is therefore desirable to investigate the split run for this type. The crystals of calcium carbonate hexahydrate used by Topley and Hume

approximated to this form, and the split run will therefore be calculated under the temperature and time conditions of Topley and Hume's experiments. An analysis of the reaction curve will first be made, allowing for nucleation as in the case of thin plates.

The Reaction Curve for Spherical Particles.

Topley and Hume assumed that the sigmoid form of the reaction curve was the result of the propagation of the reaction from one nucleus per particle, the interface at first increasing and then decreasing. It is more probable, in view of the experiments on thin plates, that the form of the curve is determined by the fact that all the crystals are not nucleated at the same time. An analysis will therefore be made on the assumption that spherical particles nucleate according to a probability law, and that once the reaction at a nucleus has started it spreads instantaneously over the entire surface of that particle, and is then propagated inwards as a spherical interface *. On this view, the "straight" portion of the curve does not occur at comparable points at different temperatures.

Let there be n_0 spherical particles of radius a, of which n_t are not nucleated at time t. Then $\frac{dn_t}{dt} = -kn_t dt$, $n_t = n_0 e^{-kt}$.

At any time t, $k.n_t.dt$ particles are nucleated during an interval dt. At a time t_2 the volume of resultant formed from these particles is

$$kn_t \left\{ \frac{4}{3}\pi a^3 - \frac{4}{3}\pi[a - u(t_2 - t)]^3 \right\} .dt.$$

Hence the fractional decomposition α, considering all the crystals which have nucleated up to time t_2, is given by

$$\alpha = \int_0^{t_2} \cdot \frac{k}{a^3} \cdot e^{-kt} \left\{ a^3 - [(a - ut_2) + ut]^3 \right\} dt$$

$$= k \int_0^{t_2} e^{-kt}.dt - \frac{k}{a^3} \int_0^{t_2} (b + ut)^3 e^{-kt} dt, \qquad \text{where } b = a - ut_2$$

$$= -\left[e^{-kt} \right]_0^{t_2} + \frac{1}{a^3} \left[\left\{ (b + ut)^3 + \frac{3u}{k}(b + ut)^2 + \frac{6u^2}{k^2}(b + ut) + \frac{6u^3}{k^3} \right\} e^{-kt} \right]_0^{t_2}.$$

* It is not implied that preparations observed microscopically by Topley and Hume had not a slower rate of surface-spreading, since small differences in the mode of preparation produce crystals of different habit and different stability.

When $t=t_2$, $b+ut=a$, and when $t=0$, $b+ut=a-ut_2$. Hence

$$\alpha = 1+\left[\frac{3u}{ka}+6\left(\frac{u}{ka}\right)^2+6\left(\frac{u}{ka}\right)^3\right]e^{-kt}$$

$$-\left[\left(\frac{a-ut}{a}\right)^3+\frac{3u}{ka}\left(\frac{a-ut}{a}\right)^2\right.$$

$$\left.+6\left(\frac{u}{ka}\right)^2\left(\frac{a-ut}{a}\right)+6\left(\frac{u}{ka}\right)^3\right], \quad \text{(I.)}$$

on dropping the subscript 2 in t_2.

When k is infinite, the above expression reduces to that for a contracting sphere, as it should, for then all particles nucleate at the start.

Equation (I.) holds up to time $t=a/u$. At this point the interfaces in particles which nucleated at zero time reach the centres and then expand, so that the values for α calculated by the above expression will be in excess of the true values. Between the times t and $t+dt$ where t is less than a/u, $k.n_0e^{-kt}.dt$ particles nucleate. At an interval of time a/u after this, the interfaces of all these particles reach the centres. The reaction, so far as these particles are concerned, then stops, but according to expression I. it goes on continuously, the interface, after reaching the centre, expanding as a sphere. Thus at time $t+a/u$, the interfaces in $k.n_0e^{-kt}.dt$ particles, according to equation (I.), begin to expand from the centre. The excess in α due to this expansion is therefore the same as would be produced by the decomposition of particles in which the reaction, instead of proceeding from the surface inwards, started at a nucleus at the centre and expanded outwards, the start of the latter reaction being a/u minutes after that of the first, and the rate of nucleation at the centre being the same as that on the surface. On subtracting the value of α for this imaginary reaction from the value given by equation (I.), we obtain the true fractional decomposition.

Hence at a time t after the same zero as before, where t is greater than a/u, $n_0.ke^{-k(t-a/u)}.dt$ points become effective in contributing to the excess, and from these at time t_2 the excess will be

$$d\alpha_{\text{excess}} = \frac{k}{a^3}.e^{-k\left(t-\frac{a}{u}\right)}u^3(t_2-t)^3.dt.$$

For all times between t_2 and a/u the excess is therefore

$$\alpha_{\text{excess}} = \frac{k}{a^3}u^3\int_{\frac{a}{u}}^{t_2}(t_2-t)^3 e^{-k\left(t-\frac{a}{u}\right)}.dt$$

$$= \frac{u^3}{a^3}\left[\left\{(t-t_2)^3+3\frac{(t-t_2)^2}{k}+6\frac{(t-t_2)}{k^2}+\frac{6}{k^3}\right\}e^{-k\left(t-\frac{a}{u}\right)}\right]_{\frac{a}{u}}^{t_2}$$

$$= \frac{6u^3}{a^3k^3}e^{\frac{k(a-ut)}{u}} - \left(\frac{a-ut}{a}\right)^3 - \frac{3u}{ka}\left(\frac{a-ut}{a}\right)^2$$

$$-6\left(\frac{u}{ka}\right)^2\left(\frac{a-ut}{a}\right)-6\left(\frac{u}{ka}\right)^3,$$

on dropping the subscript 2 in t_2. The true value of α after time a/u will be given by

$$\alpha = 1+\left[\frac{3u}{ka}+6\left(\frac{u}{ka}\right)^2+6\left(\frac{u}{ka}\right)^3\right]e^{-kt}-6\left(\frac{u}{ka}\right)^3 e^{k\left(\frac{a-ut}{au}\right)},$$

or

$$1-\alpha = \left[6\left(\frac{u}{ka}\right)^3 e^{\frac{ka}{u}}-3\left(\frac{u}{ka}\right)-6\left(\frac{u}{ka}\right)^2-6\left(\frac{u}{ka}\right)^3\right]e^{-kt}. \quad \text{(II.)}$$

Equations (I.) and (II.) give the same values of α and $d\alpha/dt$ at the time a/u; thus the expressions pass continuously into one another. The maximum velocity occurs at a time prior to a/u and not at the junction of the two curves, as is the case for flat plates[1].

A correction must be made for the fact that the true zero time may not coincide with the experimental zero. Let the time t after the true zero be $t_{\text{obs.}}+t_c$, where $t_{\text{obs.}}$ is the observational time and t_c the zero correction. Equations (I.) and (II.) then become

$$\alpha = 1+\left[\frac{3u}{ka}+6\left(\frac{u}{ka}\right)^2+6\left(\frac{u}{ka}\right)^3\right]e^{-k(t_{\text{obs.}}+t_c)}$$

$$-\left[\left(\frac{a-ut_{\text{obs.}}-ut_c}{a}\right)^3+\frac{3u}{ka}\left(\frac{a-ut_{\text{obs.}}-ut_c}{a}\right)^2\right.$$

$$\left.+6\left(\frac{u}{ka}\right)^2\left(\frac{a-ut_{\text{obs.}}-ut_c}{a}\right)+6\left(\frac{u}{ka}\right)^3\right]. \quad . \quad . \quad \text{(I.}a\text{)}$$

$$1-\alpha = \left[6\left(\frac{u}{ka}\right)^3 e^{\frac{ka}{u}}-3\left(\frac{u}{ka}\right)-6\left(\frac{u}{ka}\right)^2-6\left(\frac{u}{ka}\right)^3\right]e^{-k(t_{\text{obs.}}+t_c)}.$$

$$. \quad . \quad . \quad \text{(II.}a\text{)}$$

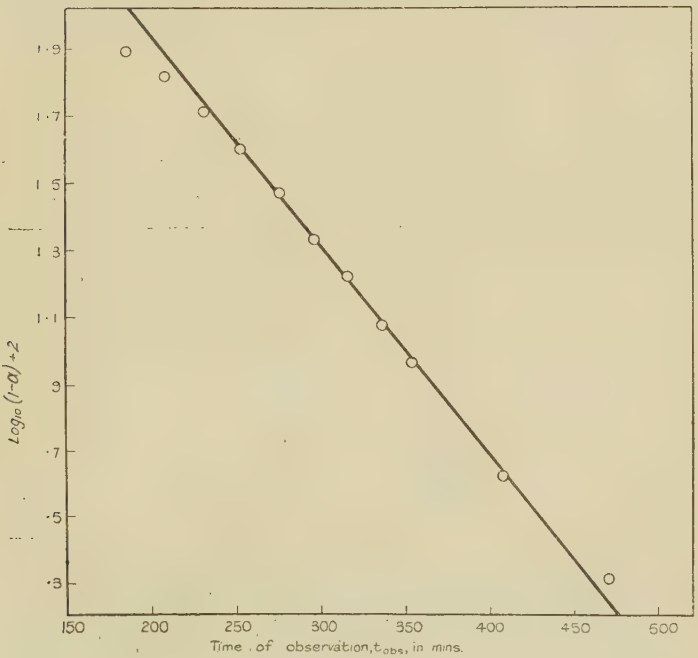
Equation (II. a) may be written in the form

$$1-\alpha = Ae^{-kt_{obs.}},$$

where

$$A = e^{-kt_c}\left[6\left(\frac{u}{ka}\right)^3 e^{\frac{ka}{u}} - 3\left(\frac{u}{ka}\right) - 6\left(\frac{u}{ka}\right)^2 - 6\left(\frac{u}{ka}\right)^3\right], \quad \text{(III.)}$$

Fig. 1.



i. e.,

$$\log_{10}(1-\alpha) = \log_{10} A - kt_{obs.} \times \cdot 4343$$

and

$$\frac{d\log_{10}(1-\alpha)}{dt_{obs.}} = -\cdot 4343\, k. \quad \text{(IV.)}$$

On plotting $t_{obs.}$ against $\log_{10}(1-\alpha)$ for the final portion of the reaction curve, a straight line should be obtained. A typical result is shown in fig. 1—data from Table I. From the graph values of A and k can be obtained.

Method of Solution and Results.

From Equation III.,

$$t_c = \frac{1}{k \times \cdot 4343}\left[\log_{10}\left\{6\left(\frac{u}{ka}\right)^3 e^{\frac{ka}{u}} - \frac{3u}{ka} - 6\left(\frac{u}{ka}\right)^2 - 6\left(\frac{u}{ka}\right)^3\right\} - \log_{10} A\right]. \quad \text{(V.)}$$

Hence t_c can be calculated for any value of u/a. Probable values of u/a, inserted in equation (V.), yield a series of values of t_c. Replacing u/a and t_c by their corresponding values,

TABLE I.

Temperature 10·48°.

$t_{obs.}$ in mins.	100 α.	$t_{obs.}$ in mins.	100 α.
0	0·00	219	43·14
50	0·20	240	54·20
97	0·76	262	66·0
118	2·79	285	75·2
128	4·57	305	81·0
140	6·60	336	88·5
154	10·41	354	91·0
175	18·27	410	95·9
195	28·68	474	98·0

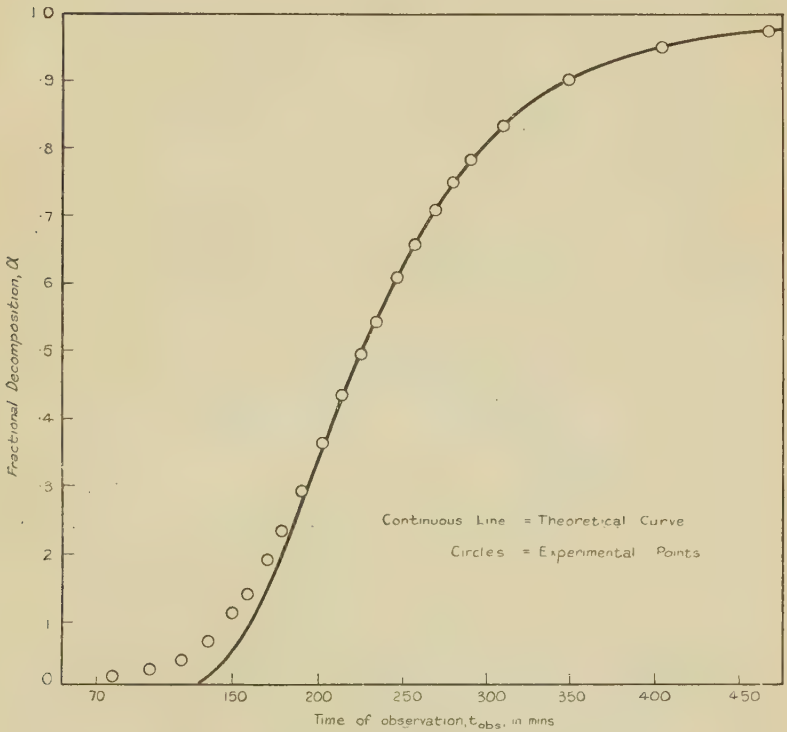
equation (I. a) gives a series of values of α for some time before a/u—the time chosen was 222 minutes. The calculated values of α are then plotted against a/u, and the value of a/u corresponding to the experimental value of α at the chosen time is read off from the graph. The correct value of t_c is then obtained from equation (V.), and points on the theoretical curve can then be calculated by equations (I. a) and (II. a).

Table I. contains some experimental results obtained with particles prepared and sized by the same methods as were employed by Topley and Hume[2]. From these data $k = 1{\cdot}428 \times 10^{-2}$ min.$^{-1}$, $a/u = 161{\cdot}5$ mins., $t_c = 136{\cdot}8$ mins. From the value of a, the radius of the particle, 8×10^{-3} cm., u is found to be $4{\cdot}95 \times 10^{-5}$ cm. min.$^{-1}$.

The theoretical and experimental curves are given in fig. 2. The agreement is good from 25 to 100 per cent.

decomposition. The discrepancy below 25 per cent. decomposition is to be expected from the nature of the assumptions regarding the *instantaneous* spreading of the reaction over the surface of the nucleated particle. Moreover, the initial part of the experimental curve is subject to uncertainty owing to extrusion of grease from the joint of the dilatometer

Fig. 2.



used[3]. This causes an apparent expansion in volume of irreproducible magnitude over a period difficult to estimate.

In fig. 1 the points plotted should diverge from the straight line before time a/u, which corresponds to $t_{obs.} = 298{\cdot}3$ minutes. This condition is satisfied, for a curve through the points bends away from the straight line at times less than this, and joins the straight line asymptotically at this point. The point of junction cannot, therefore, be read off from the graph and must be calculated as above.

Calculation of a Split Run for Spherical Particles.

In the calculation of split runs the introduction of the zero correction into the equations is unnecessary. Consider three times, t, t_1, and t_2, and suppose that the temperature is suddenly changed at t_1. From $0-t_1$ the temperature is T_1, and from t_1-t_2 it is T_2. Correspondingly we have u_1, k_1, and u_2, k_2. Suppose a particle is nucleated at time t. At t_2 the volume of resultant from this particle is

$$\frac{4}{3}\pi\left[a^3-\{a-u_1(t_1-t)-u_2(t_2-t_1)\}^3\right].$$

Hence the total volume of resultant at time t_2 produced from particles nucleating in times $0-t_1$ is

$$\int_0^{t_1}\frac{4}{3}\pi n_0 k_1 e^{-k_1 t}\left[a^3-\{a-u_1(t_1-t)-u_2(t_2-t_1)\}^3\right]dt.$$

This is of the same form as the integral from which equation (I.) is derived, except that $c+u_1t$ replaces $b+ut$, where $c=a-u_1t_1-u_2t_2+u_2t_1$.

When $t=t_1$, $c+u_1t=a-u_2(t_2-t_1)=d$, say,

$$t=0,\ c+u_1t=a-u_1t_1-u_2(t_2-t_1)=d-u_1t_1.$$

Hence the contribution to α from particles nucleating before t_1 is given by

$$\alpha_1=1-e^{-k_1t_1}+\frac{1}{a^3}\left[d^3+3\frac{u_1d^2}{k_1}+6\frac{u_1^2d}{k_1^2}+6\frac{u_1^3}{k_1^3}\right]e^{-k_1t_1}$$

$$-\frac{1}{a^3}\left[(d-u_1t_1)^3+3\frac{u_1}{k_1}(d-u_1t_1)^2+6\frac{u_1^2}{k_1^2}(d-u_1t_1)+6\frac{u_1^3}{k_1^3}\right].$$

Hence

$$\frac{d\alpha_1}{dt_2}=-\frac{u_2}{a^3}\left[3d^2+6\frac{u_1d}{k_1}+6\frac{u_1^2}{k_1^2}\right]e^{-k_1t_1}$$

$$+\frac{u_2}{a^3}\left[3(d-u_1t_1)^2+6\frac{u_1}{k_1}(d-u_1t_1)+6\frac{u_1^2}{k_1^2}\right].$$

This holds provided that t_2 is chosen so that $u_1t_1+u_2(t_2-t_1)<a$, when no correction for excess need be made.

The contribution to α from particles nucleating after time t_1, α_2, must now be calculated. At time t_1 there are $n_0e^{-k_1t_1}$ particles which have not been nucleated. The contribution from these particles is therefore obtained by replacing t by

t_2-t_1, k by k_2 u by u_2 in equation (I.), and by multiplying $e^{-k_1t_1}$. Hence

$$\alpha_2 = e^{-k_1t_1}\Big[1+\Big\{3\frac{u_2}{k_2a}+6\Big(\frac{u_2}{k_2a}\Big)^2+6\Big(\frac{u_2}{k_2a}\Big)^3\Big\}e^{-k_2(t_2-t_1)} - \Big\{\Big(\frac{a-u_2t_2+u_2t_1}{a}\Big)^3+3\frac{u_2}{k_2a}\Big(\frac{a-u_2t_2+u_2t_1}{a}\Big)^2 +6\Big(\frac{u_2}{k_2a}\Big)^2\Big(\frac{a-u_2t_2+u_2t_1}{a}\Big)+6\Big(\frac{u_2}{k_2a}\Big)^3\Big\}\Big]$$

$$= e^{-k_1t_1}\Big[1+\Big\{3\frac{u_2}{k_2a}+6\Big(\frac{u_2}{k_2a}\Big)^2+6\Big(\frac{u_2}{k_2a}\Big)^3\Big\}e^{-k_2(t_2-t_1)} - \Big\{\frac{d^3}{a^3}+3\frac{u_2}{k_2a}\cdot\frac{d^2}{a^2}+6\Big(\frac{u_2}{k_2a}\Big)^2\cdot\frac{d}{a}+6\Big(\frac{u_2}{k_2a}\Big)^3\Big\}\Big];$$

$$\therefore\quad \frac{d\alpha_2}{dt_2} = e^{-k_1t_1}\Big[-\Big\{3\frac{u_2}{k_2a}+6\Big(\frac{u_2}{k_2a}\Big)^2+6\Big(\frac{u_2}{k_2a}\Big)^3\Big\}k_2e^{-k_2(t_2-t_1)} + \frac{u_2}{a}\Big\{3\frac{d^2}{a^2}+6\frac{u_2}{k_2a}\cdot\frac{d}{a}+6\Big(\frac{u_2}{k_2a}\Big)^2\Big\}\Big].$$

The value of the tangent after changing the temperature is given by $\frac{d\alpha}{dt_2}=\frac{d\alpha_1}{dt_2}+\frac{d\alpha_2}{dt_2}$. The instantaneous tangent after splitting the run corresponds to the point $t_2=t_1$, $d=a$, $\frac{d\alpha_2}{dt_2}=0$, and is therefore

$$-\frac{u_2}{a}\Big[3+6\frac{u_1}{k_1a}+6\Big(\frac{u_1}{k_1a}\Big)^2\Big]e^{-k_1t_1} + \frac{u_2}{a}\Big[3\Big(\frac{a-u_1t_1}{a}\Big)^2+6\frac{u_1}{k_1a}\Big(\frac{a-u_1t_1}{a}\Big)+6\Big(\frac{u_1}{k_1a}\Big)^2\Big].$$

The instantaneous tangent before splitting the run is

$$-\frac{u_1}{a}\Big[3+6\frac{u_1}{k_1a}+6\Big(\frac{u_1}{k_1a}\Big)^2\Big]e^{-k_1t_1} + \frac{u_1}{a}\Big[3\Big(\frac{a-u_1t_1}{a}\Big)^2+6\frac{u_1}{k_1a}\Big(\frac{a-u_1t_1}{a}\Big)+6\Big(\frac{u_1}{k_1a}\Big)^2\Big],$$

so that, as before, the ratio of the instantaneous tangents is the ratio of the u's.

Since the measurement of the instantaneous tangent is impossible, it is of interest to determine the magnitude of the error introduced when t_2-t_1 is finite. Two cases must

be differentiated, the change from high temperature to low, and *vice versa*. The run is imagined to be split at a convenient point on the curve in fig. 2. The values of u and k at the new temperatures are calculated from the energies of activation E_u and E_k obtained in the previous paper, in conjunction with the values of u and k derived above for spherical particles.

Case I.

$T_1=10{\cdot}48°$.	$u_1=4{\cdot}95\times10^{-5}$ cm. min.$^{-1}$.	$k_1=1{\cdot}428\times10^{-2}$ min.$^{-1}$.
$T_2=7{\cdot}00$.	$u_2=2{\cdot}660\times10^{-5}$ cm. min.$^{-1}$.	$k_2=0{\cdot}748\times10^{-2}$ min.$^{-1}$.
$t_1=70$ mins.	$t_2-t_1=10$ mins.	$a=8{\cdot}0\times10^{-3}$ cm.

The instantaneous tangent is $2{\cdot}26\times10^{-3}$ min.$^{-1}$; the tangent after 10 mins. is $2{\cdot}30\times10^{-3}$ min.$^{-1}$. Thus the percentage error is only 1·77.

Case II.

$T_1=10{\cdot}48$.	$u_1=4{\cdot}95\times10^{-5}$ cm. min.$^{-1}$.	$k_1=1{\cdot}428\times10^{-2}$ min.$^{-1}$
$T_2=14{\cdot}00$.	$u_2=14{\cdot}54\times10^{-5}$ cm. min.$^{-1}$.	$k_2=2{\cdot}704\times10^{-2}$ min.$^{-1}$.
$t_1=70$ mins.	$t_2-t_1=10$ mins.	$a=8{\cdot}0\times10^{-3}$ cm.

The instantaneous tangent is $1{\cdot}98\times10^{-2}$ min.$^{-1}$; the tangent after 10 minutes is $1{\cdot}54\times10^{-2}$ min.$^{-1}$. Thus the percentage error is 22·2

The split run method for determining E_u is always sound for instantaneous tangents and for experimental conditions on proceeding from a high to a lower temperature. Nevertheless the probable percentage error in the tangent at the lower temperature may be large owing to the lowness of the slope. Analysis of the reaction curve in terms of progressive nucleation is to be preferred, in that it removes these difficulties and in addition supplies information regarding E_k.

In conclusion, the authors wish to express their thanks to Professor R. Whytlaw Gray, F.R.S., for his continued interest in this work.

References.

(1) Bradley, Colvin, and Hume, Proc. Roy. Soc. A, cxxxvii. p. 531 (1932).
(2) Topley and Hume, Proc. Roy. Soc. A, cxx. p. 211 (1928).
(3) Hume and Topley, Proc. Leeds Phil. Soc. i. p. 169 (1927).

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18 July, 1932.

CXIV. *The Magnetic Susceptibilities of some Paramagnetic Substances.* *By* W. Sucksmith (*H. H. Wills Physical Laboratory, University of Bristol* *).

THE following is an account of some measurements on the magnetic susceptibilities of some substances which have been carried out over a range of temperatures. These measurements were undertaken in order to examine the extent to which recent theoretical views † were supported by experimental data.

The writer has pointed out elsewhere ‡ the necessity for making measurements over as large a temperature range as possible, and for this purpose it is desirable to make observations both below and above room temperatures, if possible without removing the specimen under investigation from the apparatus This is particularly important when small deviations from the Curie-Weiss law $\chi(T+\Delta)=$constant, are being studied. Hitherto, most apparatus for the measurement of susceptibilities is of such a form that a different type of support is necessary in changing from the range below room temperature to that above. In general, the substance is placed in the position at which $H dH/dx$ is a maximum, so that the error due to accidental displacements from this position is reduced to a minimum. However, the volume over which this maximum value of the force due to the field-gradient is of necessity small, and the transfer of a specimen from one type of support to another—which may have a different susceptibility—will often introduce unnecessary errors. The writer has used a method previously described § and adapted it to be suitable for these measurements.

In this method the displacements due to the non-uniform field acting on the specimen are kept very small (of the order 10^{-3} cm.), so that the necessity of using a restoring force is eliminated. The small displacement of the substance is magnified to a suitable value and is thus directly proportional to the force acting on the system.

The specimen itself is supported by a circular ring of strip-phosphor bronze (see fig. 1 (not to scale)) which is

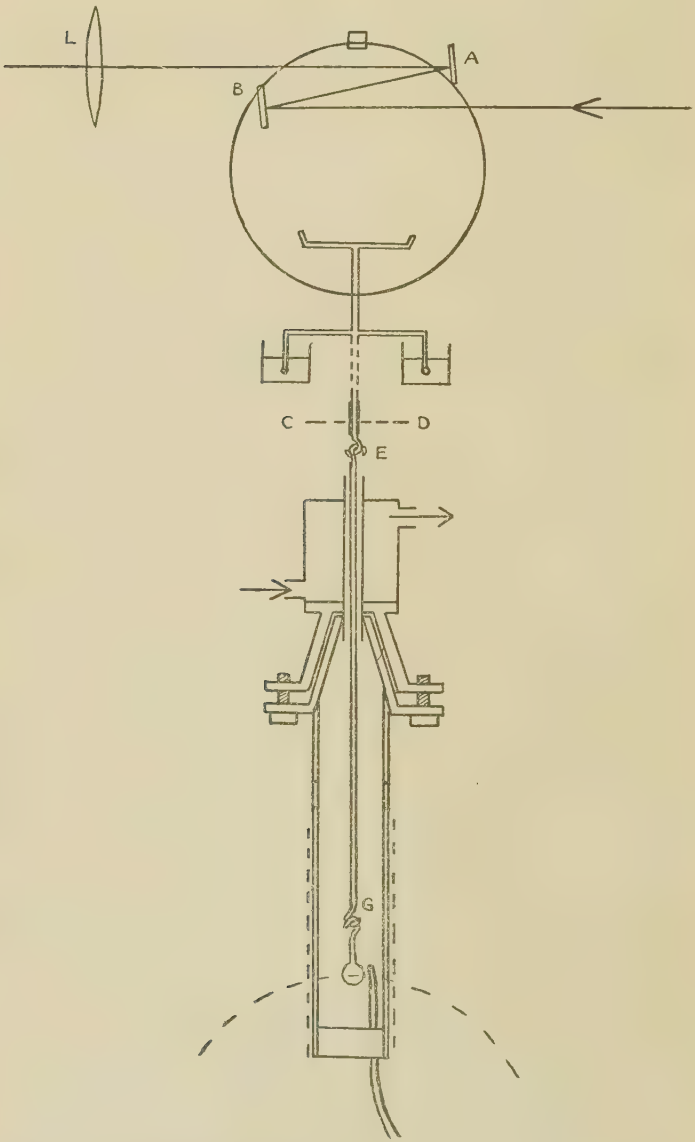
* Communicated by the Author.

† E. C. Stoner, Phil. Mag. viii. p. 250 (1929). J. H. Van Vleck, Phys. Rev. xxxii. p. 587 (1928); xxxiv. pp. 1495 and 1625 (1929).

‡ W. Sucksmith, Proc. Phys. Soc. xlii. p. 385 (1930).

§ W. Sucksmith, Phil. Mag. viii. p. 158 (1929).

Fig. 1.



fixed in a vertical plane at its highest point. The applied force due to the action of the magnetic field on the substance

under investigation elongates the ring. Light from a horizontal metal-filament lamp passes through the lens L, and falls in turn on the mirrors A and B, and thence to the image-plane of a travelling microscope with vertical traverse about a metre away.

The displacement of the image is given by

$$v = \frac{0{\cdot}561(4\mathrm{D}+2d)r^2 f}{4\mathrm{EI}}$$

$$= \frac{0{\cdot}140(4\mathrm{D}+2d)r^2}{\mathrm{EI}}\chi_m \mathrm{H}\frac{d\mathrm{H}}{dx},$$

where f = force acting on the specimen ;

d = distance between the mirrors A and B ;

D = distance of the mirror B to the microscope ;

r = radius of the phosphor-bronze ring of Young's modulus E and of inertia of cross-section I. ;

χ_m = mass susceptibility of the substance of mass m ;

and H = the magnetic field, and $d\mathrm{H}/dx$ the field gradient measured in the direction of motion of the specimen.

The apparatus has been adapted from its original form by Dr. L. C. Jackson, of this laboratory, for measurements on the directional properties of paramagnetic substances at low temperatures. In addition, the lateral constraint has been improved by the use of a flat spiral spring of phosphor bronze, which prevents motion in any but the required direction. The decrease in sensitivity is only a few per cent., and the linear relationship between force and displacement is accurately maintained. Since measurements are invariably made by comparison with a standard substance, none of the advantages of the method are lost.

In the present form a thin circular ring of wire immersed in a suitable oil provides the necessary damping. A quartz rod (0·1 cm. diameter) carrying the flat spiral spring CD is attached to the lower end of the ring and terminates in a hook at E. On this hook hangs a second quartz rod which passes through a water jacket of which the inside tube is of thin copper (3 mm. internal diameter). This jacket carries below it a brass ground joint, to which can be fixed the enclosing tube necessary for high- or low-temperature measurements without removing the phial containing the

specimen which hangs from G. The upper hook is permanently sealed as soon as the system is levelled, and the lower joint fixed with a suitable cement prior to taking measurements with a particular phial.

For high temperatures the ground joint is brazed to a silver tube, which is closed at its lower end by a piece of solid copper. The winding consists of a single layer of nickel-chrome tape, being insulated from the silver tube by a thin layer of asbestos paper. For further heat insulation for the interstices of the winding and the outside of the furnace a paste of china-clay and water-glass was used. The quantity of asbestos must be kept to a minimum owing to its strongly paramagnetic properties. A platinum-(platinum and 10 per cent. rhodium) thermocouple passes through holes in the copper plug, arranged so that the junction is as close to the position of the substance as possible. The thermal E.M.F.'s are measured on a thermocouple potentiometer.

For low temperatures a similar ground joint is attached to a length of german silver tubing which, in turn, is brazed to a copper tube closed at the bottom end. This can be enclosed in a dewar flask containing liquid oxygen, etc.

The sensitivity employed was such that 1 dyne produced 14 divisions deflexion ($v=0{\cdot}14$ mm.). Under these conditions the deflexion per milligram of $MnSo_4 . 4H_2O$ of mass susceptibility $\chi=66{\cdot}1\times10^{-6}$ at 16·2° C., was 28·5 divisions for the field and gap employed throughout. This was found to be a suitable sensitivity for susceptibilities of 2×10^{-6} and upwards. The constancy of the mechanical calibration can always be checked by loading the system and measuring the resulting deflexion. The variation of such deflexions under a given weight were found to be only slightly affected by changes of temperature, the extreme variation of room temperature being covered by $\pm0{\cdot}3$ per cent.

The substances on which measurements were carried out divide themselves into two classes, some oxides of the rare earth group, and, secondly, some uranium and molybdenum compounds.

In the first group the trioxides of Neodymium, Samarium, Europium, and Ytterbium were investigated *. The results on Yb_2O_3 are given in Table I., in which are given the absolute temperature T, the molecular susceptibility χ_M, and the product $\chi_M(T+90)$. Between 300° K. and 600° K.,

* All the oxides were obtained from Adam Hilger Ltd., and were of a high degree of purity.

the measurements show results very similar to those obtained by Cabrera and Duperier *. If $1/\chi$ is plotted against T, the curve shows a slight convexity towards the T axis above room temperature. On the other hand, continuation of the curve to lower temperatures shows a slight inflexion around

TABLE I.—Yb_2O_3.

T.	$\chi_M \times 10^6$.	$\chi_M(T+90)$.
90°	15750	2·84
198	8850	2·55
291	6640	2·53
356	5630	2·52
397	5200	2·52
431	4820	2·51
486	4370	2·51
524	4090	2·51
578	3750	2·51
652	3350	2·49
727	3010	2·46

TABLE II.—Nd_2O_3.

T.	$\chi_M \times 10^6$.	$\chi_M(T+40)$.	$\chi_M T$(theor.).
90°	12100	1·58	1·65
198	6580	1·57	1·65
290	4790	1·58	1·67
395	3670	1·60	1·69
495	3030	1·62	1·71
577	2680	1·66	1·74
655	2400	1·67	1·78

300° K., the curve becoming concave towards the T axis, apparently bending towards the origin.

The results of Nd_2O_3 are given in Table II. As in Cabrera's results, the curvature of the $1/\chi$—T curve is opposite to that of Yb_2O_3, but is more pronounced. The

* Cabrera and Duperier, *Comptes Rendus*, clxxxviii. p. 1640 (1929).

curvature is indicated by the third column which gives the product $\chi_M \cdot (T+40)$. The last column in Tables II., III., and IV. gives the molecular susceptibilities calculated from Van Vleck's theory. It is seen that the product is appreciably constant up to 300° abs. where the curvature sets in, and increases up to the highest temperatures employed.

TABLE III.—Sm_2O_3.

T.	$\chi_M \times 10^6$ (expt.).	$\chi_M \times 10^6$ (theor.).
90°	2040	1670
198	1430	1160
291	1250	1010
361	1145	1000
458	1120	980
554	1095	1000
645	1095	1010
740	1100	1030

TABLE IV.—Eu_2O_3.

T.	$\chi_M \times 10^6$ (expt.).	$\chi_M \times 10^6$ (theor.).
90°	6130	7100
198	5570	5970
294	4750	4870
348	4310	4450
368	4190	4300
426	3850	3950
527	3340	3550
618	3100	3250
673	2960	3100

Measurements on Sm_2O_3 are given in Table III. columns 1 and 2. Cabrera * has measured the susceptibility of his oxide above room temperature and found a minimum value at about 400° K., χ_M being 950×10^{-6}. The writer finds the minimum very flat at 600° K. with $\chi_M = 1010 \times 10^{-6}$.

* See 'Electric and Magnetic Susceptibilities,' Van Vleck, p. 250 (Oxford Press, 1932).

The variation of the susceptibility of Eu_2O_3 with temperature is given in fig. 2 and Table IV. It is seen that at 90° K. the susceptibility shows signs of approach to a value independent of temperature.

The second group of substances were the salts of molybdenum and uranium. Of the former metal the majority of the paramagnetic salts are unstable, and measurements were only attempted on two of these. The first was $MoCl_5$, which

Fig. 2.

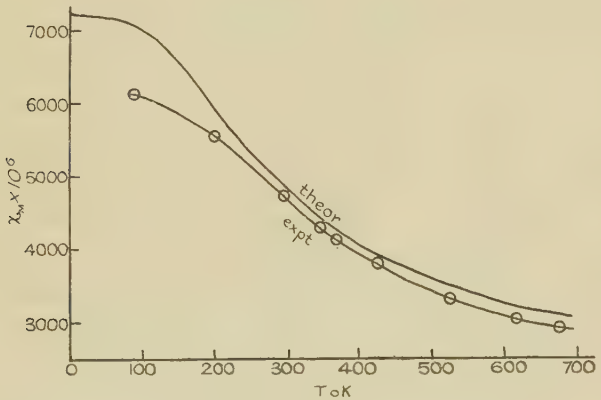


TABLE V.—UCl_4.

T.	$\chi_M \times 10^6$.	$\chi_M T$.
90°	10580	0·952
198	4880	0·965
273	4130	1·130
289	4100	1·185

was unstable in air and was sealed in a pyrex phial. The molecular susceptibilities at 90° K., 198° K., and 281° K. were respectively 3600, 1260, and 860×10^{-6}. Heating above room temperature caused irreversible changes. $MoCl_3$ is also unstable and gave only a small and variable paramagnetism. On one particular sample the values at 90° K., 198° K., and 290° K., were 1600, 490, and 270×10^{-6} respectively. These values can only be taken as approximate. In the case of the uranium compounds, measurements on UCl_4 gave results similar in type to the $MoCl_5$ mentioned above. The results are given in Table V., the two lowest

temperature-readings following the Curie law $\chi T = \text{constant}$. Above room temperature the substance was obviously unstable.

The results on UO_2, prepared by heating the oxide U_3O_8 in an atmosphere of hydrogen at about 750° C., are shown in Table VI. The Curie law is followed very closely between 90° K. and 430° K., Δ being equal to 310°. The oxides UO_3 and $UO_2(NO_3)_2$ both proved to be diamagnetic, and the results are therefore omitted.

TABLE VI.—UO_2.

T.	$\chi_M \times 10^6$.	$(\chi_M 10^6)(T+310)$.
90°	5960	2·39
198	4700	2·39
290	3960	2·38
370	3510	2·39
430	3210	2·38
499	2750	2·22
548	2430	2·09

TABLE VII.—$U(SO_4)_2$.

T.	$\chi_M \times 10^6$.	$\chi_M(T+85)$.	$\chi_M \times 10^6$.	$\chi_M(T+128)$.
90°	7310	1·285	5650	1·233
198	4590	1·300	3820	1·245
290	3460	1·205	2980	1·250
368	2860	1·295	2520	1·251
427			2260	1·253
516			1900	1·228
593			1725	1·244

The salt $U(SO_4)_2$, which crystallizes with the varying number of water molecules between one and nine, was prepared by dissolving U_3O_8 in sulphuric acid and crystallizing from alcoholic solution. None of the specimens gave integral numbers of water molecules, and measurements were taken with different degrees of hydration. The results of a specimen containing 4·1 molecules of water and the same dehydrated are given in the second and fourth columns of Table VII. The Curie constants agree fairly closely, and $\Delta = 85°$ and 128° respectively.

Discussion of Results.

The theory of Van Vleck has met with particular success in explaining the magnetic properties of this group. The $4f$ electrons are responsible for the paramagnetism, and being screened from external influence by the closed sub-group of $5s$ and $5d$ electrons are apparently as free, as far as orientation is concerned, as if they were in the gaseous state.

The molecular susceptibility is given by

$$\chi_{\mathrm{M}} = \frac{\mathrm{N}\Sigma_j\{g^2\beta^2 j(j+1)/3k\mathrm{T} + \alpha(j)\}(2j+1)e^{-\mathrm{W}_j/k\mathrm{T}}}{\Sigma_j(2j+1)e^{-\mathrm{W}/k\mathrm{T}}}$$

where $g =$ the Landé splitting factor;

$\beta =$ the Bohr magneton $= eh/4\pi mc$;

and $\mathrm{W} = hc\Delta\nu =$ the difference in energy between the particular j-level and the ground-level.

The term $\alpha(j)$ is due to the component of magnetic moment perpendicular to the angular momentum vector, and is, in general, negligible. However, the distribution of ions amongst the different j-levels varies with temperature, and in the first half of the group, where the multiplets are erect, the Bohr magneton number, $\mu_{\mathrm{B}} = (3k\mathrm{T}\chi_j/\mathrm{N}\beta^2)^{\frac{1}{2}}$ increases with temperature, so that the slope of the $1/\chi - \mathrm{T}$ curve decreases with temperature. In the second half of a group, the multiplets are inverted, and all levels except the ground-level are practically unoccupied at all obtainable temperatures. In this case the equation simplifies to a single term, and the ions coming under this classification, *e.g.*, Yb^{+++} should, in the gaseous state, follow the Curie law. The deviations from this law, together with the fact that the modified law $\chi(\mathrm{T}+\Delta) =$ constant, is often obeyed, is usually ascribed to interatomic forces, which would be expected to be larger for Yb_2O_3 than for $Yb_2(SO_4)_3$. Cabrera and Duperier* find the greater curvature of the $1/\chi - \mathrm{T}$ curve occurs for the anhydrous sulphate. It would be interesting to know if the double curvature shown by the oxide is also followed by the sulphate, but its rarity prevents inclusion in the present work.

Nd_2O_3, above room temperature, shows an opposite curvature when $1/\chi$ is plotted against T, in general accord with the Van Vleck formula. The curve is practically straight below room temperature, with the curvature

* *Loc. cit.*

increasing with temperature, in good agreement with theory (see Table II.). The actual numerical values of the molecular susceptibility at room temperature differ rather considerably. Cabrera's value being 4910, the calculated value 5750, whilst the present measurements give 4790×10^{-6} *.

The ions Sm^{+++} and Eu^{+++} differ from others in that the $\alpha(j)$ term of the theoretical formula is considerable, and the changes of susceptibility with temperature are widely different from others of this group. The variation of the magnetic and thermal properties of these ions have been discussed by Frank †. The most noticeable feature of Eu^{+++} is the approach to a constant value of χ as the lowest temperatures are reached. The theoretical relationship between susceptibility and temperature is shown in the upper curve of fig. 2, the observed values being represented by circles. The approach to a constant value for χ is quite appreciable at 90° K. and should be complete below 50° K., so that measurements at liquid hydrogen temperatures are desirable to confirm this.

In Sm^{+++} the existence of a minimum value for χ is predicted between 380° K. and 450° K. Cabrera has found such a minimum between 350° and 425°, whilst the present measurements show a comparatively flat region extending to higher temperatures. It is seen from Table III. that the increase at low temperatures is not so great as would be expected theoretically.

Measurements on the remaining substances were undertaken to ascertain whether the view held by Stoner ‡ with regard to ions in the first transition series was followed for paramagnetic substances outside this group. In all paramagnetic ions, with the exception of the rare earth group, the electrons responsible for paramagnetism are not screened from forces due to neighbouring atoms by a closed diamagnetic shell. If there is atomic interaction we might expect the orbital moment to be wholly or partially suppressed. Evidence for this view is found in the susceptibility data for other ions of the iron group and also by measure-

* An examination of the results of Cabrera and Duperier shows that the curvature of the $1/\chi$—T relationships above room temperature is opposite in the second half of the group to that in the first half. Whilst the latter is fully explained by the fact that, owing to the Boltzmann factor, the magneton number increases with temperature for the erect terms, no theoretical reasons have been advanced for the opposite curvature in the second half. Possibly the double curvature shown by Yb_2O_3 is general for the second half of the group.

† Phys. Rev. xxxix. p. 119 (1932).

‡ *Loc. cit.*

ments of the gyromagnetic ratio by the writer on the Co^{++}, ion *. Both susceptibility and gyromagnetic results show that for this ion the orbital moment is partially suppressed. Unfortunately, the magnitude of the gyromagnetic effect for the substances mentioned below is too small to admit of sufficiently accurate measurement.

$MoCl_5$, having one $4d$ electron, should have an effective Bohr magneton number of 1·73 if spin moment alone is effective, or 1·55 if the state is ^2D (Russell-Saunders coupling). Owing to the variation of the Curie constant over the temperature range it is impossible to calculate the magneton number, but the limits can be given as 1·54–1·65.

$MoCl_3$, with three $4d$ electrons, should have a Bohr magneton number 3·85 if spin moment alone were effective, the susceptibility being smaller if the orbital moment were effective. It would appear that this latter view is in better agreement with the present data, but other experiments rather tend to negative this.

During the preparation of the paper an advance note by Tjabbes † has appeared in which he has made a study of a number of molybdenum salts at room temperature. The two above results are in fair agreement with his data for those salts. However, results on the more stable complex salts, together with those of Bose and Bhar‡, who measured the susceptibility of similar compounds at room temperature, give magneton numbers in agreement with the spin hypothesis. Further, the temperature variation of the two chlorides mentioned above tends to support this view. The effect of interatomic forces is evidently so strong that the ionic moments are suppressed to such an extent as to prevent agreement with any of the existing theories.

In the case of the uranium salts the results on $U(SO_4)_2$, with two $6d$ electrons, are the only ones suitable for adequate theoretical comparison. For the two examples given the magneton numbers are 3·20 and 3·17 respectively, other specimens giving similar results. The theoretical value for similar configurations in the iron group vary from 2·8 to 3·4. Further, the modified Curie law holds, which supports the spin hypothesis, so that here one finds reasonably good agreement. The chloride UCl_4 has also two $6d$ electrons available. It follows the Curie law approximately up to 198° K., but the product χT increases above this temperature. Above room temperature it is unstable. The magneton

* W. Sucksmith, Proc. Roy. Soc. cxxxiii. p. 179 (1931).
† B. Th. Tjabbes, Proc. Amst. Acad. xxxv. p. 693 (1932).
‡ *Zs. für Phys.* xlviii. p. 716 (1928).

number deduced from the lowest temperatures gives 2·76 magnetons.

The two above results indicate that spin moment only is responsible for the paramagnetism of the U^{++++} ion.

Summary.

A description is given of an apparatus for the measurement of magnetic susceptibilities at temperatures above and below room temperature. The deflexions are kept very small, so that a linear relationship exists between the deflecting force and the resulting displacement.

Results of measurements on same oxides of the rare earth group and also on salts of molybdenum and uranium are given. The measurements on the rare earth group are in strong confirmation of the theory of Van Vleck, whilst the data on molybdenum and uranium salts lend support to the view that the paramagnetism of these substances is due to spin moment only.

CXV. *On the Generation of Ultra-short Electromagnetic Waves using the Scheme of H. Barkhausen and K. Kurz.* *By* G. Potapenko, *Professor of Physics, Mining Academy of Moscow; Carnegie Fellow, Norman Bridge Laboratory of Physics, California Institute of Technology, Pasadena* *.

§1. In 1920 H. Barkhausen and K. Kurz † proposed a new method of producing ultra-short undamped electromagnetic waves. The method makes use of the electronic oscillations which originate within a vacuum tube when high positive potentials are impressed on the grid with respect to the filament and the plate. A large number of papers dealing with this method have appeared during recent years ‡. The results are at times contradictory and some of the details remain obscure. Nevertheless, enough material has been gathered to permit us to draw, with a fair degree of certainty,

* Communicated by Prof. R. A. Millikan.

† H. Barkhausen and K. Kurz, *Physik Zeits.* xxi. pp. 1–6 (1920).

‡ See for summaries: H. E. Hollmann, *Zeits. f. Hochfr.* xxxiii. pp. 27–30, 66–74, 101 107 (1923), xxxv. pp. 21–27, 76–80 (1930); K. Kohl, *Erg. d. ex. Naturwiss*, ix. pp. 275–341 (1930). A few of the more recent papers will be mentioned below.

a general scheme of the phenomena of the production of ultra-short waves, and of the electronic processes which take place within the vacuum tube.

Using the scheme of H. Barkhausen and K. Kurz the vacuum tube can generate oscillations of two kinds, differing with respect to the oscillating circuits with which the tubes can be coupled.

BK-*oscillations*.—Their wave-length λ does not depend on the natural periods of the oscillating circuits coupled with the tube and is determined from the equation

$$\lambda = c_0\tau, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where c_0 is the velocity of light and τ is the period of electronic oscillations about the grid of the tube, or, in other words, the time it takes the electrons to pass from the filament to the plate and back to the filament. The time τ can approximately be computed from the dimensions of the electrodes of the tube and from the values of the potentials. If the potential at the plate is equal to zero or if it is small in comparison with the potential at the grid Eg, formula (1) can be written as follows :—

$$\lambda^2 \mathrm{E}g = \mathrm{Const}_0. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In this equation, frequently called Barkhausen's equation, the value of Const_0 is a function of the dimensions of the tube*. According to what was said before, in the case of BK-oscillations, Barkhausen's equation will be satisfied at all values of the natural period of the oscillating circuit coupled with the tube. Oscillations of this type have been observed only in a very few cases †; their intensity was found to be comparatively very low, several times lower than the intensity of oscillations

* The numerical value of Const_0 can be calculated from the formulæ : H. Barkhausen and K Kurz, *loc. cit.*; S. Zilitinkiewitch, *Drahtl. Tel. u. Tel.* (Russ.) xviii. pp. 2–22 (1923), xix. pp. 166–175 (1923); *Arch. f. Elektrot*, xv. pp. 470–484 (1926); A. Scheibe, *Ann. d. Physik*, lxxiii. pp. 54–88 (1924).

† The most certain are the observations of : N. Kapzov & S. Gwosdower, *Zeits. f. Phys.* xlv. pp. 114–134 (1927); H. E. Hollmann, *Ann. d. Physik*, lxxxvi. pp. 129–260 (1928). The nomenclature of the waves which we use was proposed by H. E. Hollmann. Unfortunately this nomenclature has not yet found universal acceptance. Sometimes the name BK is used to designate all kinds of waves which are generated at large positive grid potentials without definitely stating what kind of waves are actually observed.

of the other type. As a result, BK-oscillations have been very little studied so far.

GM-*oscillations*.—These are characterized by the fact that the length of the waves depends on the natural periods of the oscillating circuits coupled with the tube. Thus, in this case, Barkhausen's equation is satisfied only at such voltages E*g* and at such natural periods of the oscillating circuits which correspond to the maximum energy of oscillations *. In other words, in the case of GM-oscillations, the Barkhausen equation is satisfied only when quite definite relationships exist between the natural period of the oscillating circuits and the period of electronic oscillations. Oscillations of this type are the ones usually observed, and they have been studied more thoroughly than BK-oscillations.

We had shown † that GM-oscillations can give rise to several kinds of waves. The length of some of them satisfies equation (1), provided the condition of maximum oscillation energy is satisfied; in other words, the wave-length corresponds to a complete period of electronic oscillations. We called these waves "normal waves." A number of other waves can also be observed; if the energy of oscillations is kept at a maximum, their wave-length satisfies one of the following equations

$$\lambda=c_0\frac{\tau}{2},\quad \lambda=c_0\frac{\tau}{3},\quad \lambda=c_0\frac{\tau}{4}. \quad . \quad . \quad . \quad . \quad (3)$$

These waves of higher orders were called "dwarf waves" of the 1st, 2nd, 3rd . . . orders depending on the equation they satisfy. This name was chosen in view of the fact that the length of these waves is many times, sometimes almost 30 times, shorter than the length of normal waves, which should be generated by the tube at the corresponding voltages E*g*. All the dwarf waves belong to the type of GM-oscillations. Barkhausen's equation is satisfied under the same conditions as in the case of normal waves; the values of the product λ^2E*g*, however, was found to be a definite number of times smaller than

* Provided that the heating current is kept constant and under certain other restrictions which will be spoken of below.

† G. Potapenko, *Zeits. f. tech. Physik*, x. pp. 542–548 (1929); Phys. Rev. xxxix. pp. 625–637, 638–665 (1932).

in the case of normal waves. With a sufficient degree of accuracy it satisfied the equation

$$\lambda^2 E g = \frac{\text{Const}_0}{n^2}, \quad \ldots\ldots \quad (4)$$

which is an obvious consequence of eqs. (1), (2) and (3). Here n is an integer, the case $n=1$ corresponding to normal waves, and the cases $n=2, 3, 4 \ldots\ldots$ to dwarf waves. From the view-point of the motions of the electrons, the difference between normal and dwarf waves is that the frequency of the normal waves corresponds to the frequency of electronic oscillations, and the frequency of dwarf waves exceeds by an integral number of times the frequency of electronic oscillations. It should be mentioned, that in spite of the superficial resemblance of series (3) to the series of harmonic overtones, the dwarf waves are not overtones of the normal waves, and are generated quite independently of them. Only a few of the tubes which can generate normal waves are capable of producing dwarf waves. This depends, primarily, on the asymmetry in the arrangement of the electrodes of the tube; because of this asymmetry the time τ will be different for different electrons, depending on the direction of their motion inside of the tube. The problem of the symmetry in the arrangement of the electrodes was studied at our suggestion by A. Wainberg *.

§ 2. The reasons why vacuum tubes can generate oscillations of one type or another can be elucidated by investigating the conditions and the character of the electronic motions within the tubes. If the electrons were issuing from the filament at a uniform rate, and if their oscillations about the grid were disordered, in other words, if all their phases were equally possible, then no oscillations would be observable outside of the tube, for example, in one of the oscillating circuits coupled with the tube. Since in reality oscillations are observable in these circuits it becomes evident that the motions of the electrons are in some way regulated.

The question as to how these electronic motions are regulated is most intimately connected with the problem

* A. Wainberg, Journ. Appl. Phys. (Russ.) vii. pp. 97–104 (1930) see also G. Potapenko, Phys. Rev. xxxix. p. 661 (1932).

of the causes of the generation of waves of different types; it is a fundamental question in the theory of these phenomena.

If the oscillations in the circuits coupled with the tube are sufficiently intense, appreciably large alternating potentials should appear at the electrodes of the tube. E. W. Gill and J. H. Morrell * were the first to show that such potentials should cause a periodic division of the electrons into two groups, producing an increase in the velocity of some of them and a decrease in the velocity of others. This should result in a periodic change in the density of the current flowing across the tube and in a transmission of a definite amount of energy into the circuit coupled with the tube. Thus, oscillations, having once been started in the circuit, can be maintained, due to this periodic supply of energy. Quite analogously we have shown † that the divisions of the electrons into groups and the transmission of energy into the oscillating circuit must take place whenever any one of the relationships (3) is satisfied. The energy of the oscillations in the circuit and the potentials at the electrodes of the tube will have their maximum value when the natural period of the circuit approaches one of the wave-lengths given by eqs. (1) and (3). Hence it follows that tubes can transmit a maximum amount of energy into the oscillating circuit when the natural period T of this circuit is equal to the period τ of the electronic oscillations (normal waves), and also when

$$T=\frac{\tau}{2},\quad T=\frac{\tau}{3},\quad T=\frac{\tau}{4}\ \text{(dwarf waves)}.$$

The conditions

$$T=\tau,\quad T=\frac{\tau}{2},\quad T=\frac{\tau}{3},\quad T=\frac{\tau}{4},\ldots\ . \qquad (5)$$

are the conditions under which a vacuum tube can generate oscillations or the conditions of excitation of the oscillating circuit coupled with the tube. Hence it follows, incidentally, that when these conditions are satisfied the dynamic resistance of the tube must be negative. For the production of oscillations it is immaterial whether the

* E. W. Gill and J. H. Morrell, Phil. Mag. xliv. pp. 161–178 (1922).

† G. Potapenko, Phys. Rev. xxxviii. p. 548 (1931), xl. pp. 988–1001 (1932).

natural period T of the circuit will be its fundamental period or one of its overtones, since oscillations corresponding to any one of these periods can be produced in the circuit, provided the above relationship between T and τ are satisfied. The relationships (5) show, on the other hand, that the length of waves generated by the tube must always correspond to one of the natural periods (fundamental or overtone) of the oscillating circuits coupled with the tube, as it had been shown experimentally by M. Grechova *. The relationships between T and τ define in this case at which τ, and consequently at which E*g*, the excitation of oscillations in the circuit will be most probable. The relation between the length of the waves and the periods of oscillating circuits shows that these waves must correspond to GM-oscillations. Therefore a theory which explains the ordering of electronic motions by the influence of alternating potentials and all the consequences of such a theory must be applicable to GM-oscillations.

At the present time it is difficult to state definitely the reason why the electronic motions are regulated in the case of BK-oscillations when the amplitudes of the alternating potentials must be vanishingly small in comparison with the magnitude of the constant potential E*g*. According to F. Tank † and B. van der Pol ‡ this may be due to the oscillations in the density of the space charges, which must occur periodically with a period equal to the period of electronic oscillations. The oscillations in the density of the space charges must give rise to similar oscillations in the emission current, which in its turn will cause oscillations in the current flowing across the tube. The concept of the effect of the space charges cannot be considered as completely clear. M. J. O. Strutt §, for example, considers that there is no reason to assume a difference in the mechanism of BK- and GM-oscillations, which had been observed by H. Hollmann. R. King ‖ shares this opinion.

* M. Grechova, *Phys. Zeits.* xxix. pp. 727–729 (1928); see also K. Kohl, *Elekts. Nachr. Techn.* vi. pp. 354–358 (1929).

† F. Tank, *Arch. sc. phys. et natur.* vi. pp. 320–321 (1924); F. Tank & E. Schilknecht, *Helvetica phys.* Acta 1, pp. 110–138 (1928).

‡ B. van der Pol, *Physica*, v. pp. 1–8 (1925).

§ M. J. O. Strutt, *Ann. d. Phys.* iv. p. 29 (1930); see the objections of H. E. Hollmann, *Ann. d. Phys.* v. pp. 247–260 (1930).

‖ R. King, *Ann. d. Phys.* vii. p. 827 (1930).

K. Kohl * thinks that the oscillations of the circuit may play a role even in the case of BK-oscillations. W. Romanoff † believes that the difference between BK- and GM-oscillations consists in the degree of coupling of the oscillating circuit with the tube.

Irrespective of what the real cause of the ordering of the electronic motions in the case of BK-oscillations can be, we may mention that oscillations of this type can be observed only when the period of electronic oscillations and its sub-multiples (at least the nearest sub-multiples) differ considerably from the natural periods of the oscillating circuits coupled with the tube. In these cases (if we do not consider the case when the oscillating circuit is " blocked " ‡) the alternating potentials at the electrodes of the tube must be vanishingly small. It is known that under these conditions BK-oscillations have been actually observed by N. Kapzov and S. Gwosdower and H. E. Hollmann. In other cases the oscillations of the circuit must be intense, corresponding alternating potentials must appear at the electrodes, and the oscillations generated will belong to the GM-type. In intermediate cases H. E. Hollmann succeeded in observing a gradual transition from one type of oscillation to another, and within narrow limits a simultaneous co-existence of the two types. In the conditions of our work we have not succeeded so far in observing BK-oscillations. All the oscillations produced by our generator belonged to the GM-type.

§ 3. The results of our investigations show that the lengths of the dwarf waves do correspond to series (3) and (4) with a sufficient degree of accuracy. At the same time the observed lengths of the normal waves are systematically shorter, by approximately 15 per cent., than those computed from formulæ (1) and (2). This discrepancy is due to the fact that τ, the period of electronic oscillation, cannot be computed accurately at the present time. The formulæ from which it can be calculated do not take into account its dependence on the alternating potentials at the electrodes of the

* K. Kohl, *Erg. d. ex. Naturwiss.* ix. p. 268 (1930).
† W. Romanoff, *Vestnik exp. i teor. Elektrot.* (Russ.) ii. p. 80 (1929).
‡ F. Tank & Schiltknecht, *Helvetica physica*, Acta i. p. 126 (1926); H. E. Hollmann, *Ann. d. Phys.* lxxxvi. p. 171 (1928).

tube, spoken of above. Thus, the value of τ computed from these formulæ is not accurate. Investigations of the effect of the amplitude of the alternating potentials on the length of the normal and of dwarf waves * show that these potentials have a maximum effect on the length of normal waves. Furthermore, the intensity of normal waves is considerably greater than that of dwarf waves and the amplitudes of the alternating potentials corresponding to normal waves are the largest. As a result, the lengths of the normal waves, calculated from the formula (1) or (2), differ considerably from the observed values, while in the case of dwarf waves the observed values are very near to those computed from formulæ (3) and (4). Later we shall give a formula which takes into account the effect of the alternating potentials.

Investigations of the effect of the alternating potentials on the length of waves show also that the quantity τ, which enters formulæ (1) and (4) as well as the conditions of generation (5), does really correspond to a complete period of electronic oscillations about the grid or, in other words, to the time it takes the electrons to pass from the filament to the plate of the tube (or, more exactly, to the so-called surface of zero potential) and back to the filament. There is an exception to this rule when waves are generated by a tube with a close mesh grid. In such a case, the so-called "oscillations of a higher frequency" can be obtained, as was shown by H. E. Hollmann. They correspond to a shorter time of passage of the electrons τ, since the electrons, after passing through the grid, will to a great extent be detained by the grid on their way from the plate back to the filament. Together with waves, for which the values of the products $\lambda^2 Eg$ correspond to members of series (4), "oscillations of a higher frequency" can produce another series of waves † for which the products $\lambda^2 Eg$ will have a smaller value.

There is still another case when the values of the products $\lambda^2 Eg$ can be different from the members of series (4). It occurs when, in accordance with conditions

* G. Potapenko, Phys. Rev. xxxix. p. 547; xl. p. 1001; xli. pp. 216–230 (1932).

† We obtained two such series with tubes Phillips TA-0810; the average values of the products $\lambda^2 Eg$ for members of one series differed from the corresponding members of the second series by approximately 17 per cent.

(5), oscillations originate in one of the internal circuits of the tube, *i. e.*, in one of the circuits situated within the bulb or the base of the tube. In such a case oscillations can be occasionally observed in the external circuits coupled with the tube, the wave-length of which can be two or three times greater than the expected value *. They are found in those regions of the working diagram of the tube where shorter waves should be situated, of which they are the derivatives. For such waves the values of the product $\lambda^2 Eg$ will not correspond to members of series (4), since in this case the n in the denominator should be replaced by $n/4$ or $n/9$, *i. e.*, it can be equal to 0·44, 1·78, 2·25, 2·78, 6·25, etc. The paucity of experimental material makes it difficult to say how such waves can originate. Apparently they are in some way connected with an asymmetry in the generator, judging from the fact that with a careful selection of the so-called "ballast" capacity of the generator, we never observed such waves.

§ 4. We have said that the value of the product $\lambda^2 Eg$ should remain constant; in the case of BK-oscillations it must always be constant and in case of GM-oscillations it should be constant when the energy of oscillations is at a maximum. Investigations show, however, that there are still other conditions to be satisfied in order that $\lambda^2 Eg$ be constant: the heating current should be kept constant and, as we had shown for the case of GM-oscillations, the voltage Eg should be greater than that value Es which corresponds to the upper bend of the emission-grid characteristic of the tube (*i. e.* $Eg > Es$). The latter requirement is easily explained, since at voltages less than Es the effect of space charges (which are not taken into account by the above formulæ) becomes very pronounced.

In a recent paper E. W. Gill † made an attempt to generalize Barkhausen's formula for the case of a non-

* We obtained such oscillations in 1929 using tubes of the type R 5. A year later they were independently observed by I. Nekraschewitch and M. Sliosberg, using tubes of the same type (in our laboratory; work unpublished). It is of interest that in all these cases the waves obtained can be considered as derivatives of dwarf waves of the 4th order.

† E. W. Gill, Phil. Mag. xii. pp. 843–853 (1931).

constant heating current of the tube. He proposed the following formula (we use our customary notation) :—

$$\frac{\lambda^2 Ig}{\sqrt{Eg}} = \text{Const}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where λ is the wave-length of the oscillations generated. Eg the constant grid potential, and Ig the current in the grid circuit of the tube, which is a function of the heating current. This formula was derived theoretically and verified experimentally. We can test this formula using the results of our measurements given in Table I. Our measurements were made in the customary manner by means of a generator, previously described, and using a vacuum tube of the type R 5. The grid voltage was selected according to the maximum current Ia in the plate circuit of the generator, *i. e.*, it approximately corresponded to the maximum energy of the oscillations *. The observations were made in such points on the lines of maxima of the working diagram of the tube as corresponded to monochromatic oscillations. Particular pains were taken in this respect, since the working diagram of the tube used (tube No. 5, which had been tested previously) was rich in regions of dwarf waves. Thus, unless the selection of points of observation was made with particular care, waves of a different order could become admixed (as the heating current was changed) to waves of which the length was being determined. This might lead to errors in the determination of the intensity of waves. Measurements were made of normal waves and of dwarf waves of the first three orders. Table I. gives the wave-length λ, the grid voltage Eg, the grid current Ig, the length of the plate and of the grid circuits L, the heating current Ih and the plate current Ia. The observed values of λ were rounded off to 0·1 cm. for normal and dwarf waves of the 1st order. They were rounded off to 0·05 cm. for dwarf waves of the 2nd and 3rd orders, as the accuracy of the measurements was somewhat greater for shorter waves. The Table I. also contains the values of $\lambda^2 Eg$ and $\frac{\lambda^2 Ig}{\sqrt{Eg}}$, computed from the results of the measurements.

* As a matter of fact, the amplitude of the oscillations is proportional to $(Ia+a)$, where a is a correction depending on the drop of potential along the filament. At $Ia=0$ the correction $a=0$, so that the condition $Ia=0$ corresponds to a zero amplitude of oscillations.

The data of the last two columns show that the formula proposed by E. W. Gill is not supported by our observations. Of still greater importance is the fact that his formula is in poorer agreement with the observations

TABLE I.

Tube R5 (No. 5).

I_h (amp.).	E_g (volt).	I_g (m.a.)	I_a (m.a.)	λ (cm.).	$\lambda^2 E_g$.	$\frac{\lambda^2 I_g}{\sqrt{E_g}}$.
			Normal waves ; L = 23 cm.			
0·701	162	31·6	4·40	60·0	$5·83 \times 10^5$	8940
0·684	161	24·3	3·75	60·6	5·91 „	7030
0·662	160	16·1	2·90	61·0	5·95 „	4740
0·651	161	12·8	2·25	61·3	6·05 „	3790
0·640	162	10·3	1·75	61·6	6·15 „	3000
0·632	165	8·7	1·30	61·8	6·30 „	2590
0·625	167	8·0	0·90	62·0	6·42 „	2380
0·610	169	6·7	0·30	62·4	6·58 „	2010
			Dwarf waves, 1st order ; L = 13 cm.			
0·701	152	34·3	2·70	36·6	$2·04 \times 10^5$	3900
0·684	146	26·3	2·20	37·0	2·00 „	2970
0·662	138	18·1	1·80	37·3	1·92 „	2140
0·651	136	14·7	1·30	37·2	1·88 „	1740
0·640	133	12·2	0·85	37·0	1·82 „	1450
0·625	127	9·3	0·30	36·8	1·72 „	1120
			Dwarf waves, 2nd order ; L = 6 cm.			
0·701	240	38·0	2·00	18·85	$0·852 \times 10^5$	872
0·684	234	28·4	1·60	18·9	0·836 „	663
0·662	228	20·2	0·80	18·8	0·806 „	473
0·651	224	17·0	0·50	18·7	0·783 „	397
0·640	221	13·8	0·20	18·55	0·760 „	319
0·625	217	10·2	0·02	18·4	0·735 „	234
			Dwarf waves, 3rd order ; L = 8 cm.			
0·701	305	43·6	0·95	12·7	$0·492 \times 10^5$	403
0·684	300	33·4	0·65	12·55	0·473 „	304
0·674	288	29·2	0·35	12·5	0·450 „	269
0·662	278	21·9	0·10	12·5	0·434 „	205

than the usual formula (2), of which it was supposed to be a generalization for any values of I_g and E_g. This result holds true both for normal and for dwarf waves of all orders. The very nature of the discrepancy between our results and Gill's results precludes any possibility of ascribing it to accidental errors of measurement. Because of a lack of experimental material it is difficult

to decide what the causes of this discrepancy are. We may suggest, however, that in all probability it is due to a difference in the vacuum of the tubes. As E. W. Gill mentions, his tube had a poor vacuum giving ionization current at voltages as low as $Eg = 157v$. All the tubes which we had at our disposal had a good vacuum. The tube with which we obtained the results presented in Table I. gave no measurable ionization current up to $Eg = 550$–$600v$.

§5. There are several reasons why the length of the waves changes as the heating current is changed. One of the possible causes is a change in the density of the space charges which produces a change in the time of passage of the electrons, or, according to a theory recently proposed by A. Rostagni *, a change in the natural period of these charges. In the second place it may be due to transitions of normal waves into dwarf waves and *vice versa*. Such transitions should be accompanied by sudden changes in the wave-length. They have been found experimentally by W. J. Kalinin †. Finally, it may be due to the effect of alternating potentials which must be present at the electrodes of the tube during oscillations, and the amplitude of which must change as the heating current is changed. The effect of the change in the amplitude of the alternating potentials on the length of the normal and of the dwarf waves has been studied theoretically by P. S. Epstein ‡.

The measurements presented in Table I. were made at voltages $Eg > Es$. This, in our opinion, precludes the possibility of explaining the change in the length of waves as being due to the effect of the change of the density of the space charges on the time of passage of the electrons, since at $Eg > Es$ this effect must generally be negligible. Nor can we accept the explanation proposed by A. Rostagni, since according to his theory the wave-length should increase as the heating current is decreased. Our measurements show, however, that this is true only in the case of normal waves, while in

* A. Rostagni, *Atti della R. Acad. di Torino*, xvi. pp. 123–130, 217–223, 383–395 (1931).

† W. J. Kalinin, *Ann. d. Phys.* xi. pp. 113–128 (1931).

‡ P. S. Epstein, Report at the Physics Research Conference, Pasadena (March 5, 1931).

the case of dwarf waves we observe an opposite effect. It is also evident that in our measurements there could be no transitions from one kind of waves to another. There remains the last explanation—the effect of a change in the amplitude of the alternating potentials. The theory of P. S. Epstein shows that a change in the amplitude of alternating potentials must have a different effect on different kinds of waves. The length of the normal waves should increase and the length of the dwarf waves should decrease as the amplitude is decreased. As can be seen from Table I., this is in complete agreement with the results of our measurements.

So far we have not had the opportunity of making a detailed verification of the explanation proposed by P. S. Epstein; we shall give, however, a very simple approximate formula, which gives a sufficiently clear idea of the relationship between the length of waves and the plate current Ia, and consequently the heating current of the tube.

As we have mentioned earlier, the current Ia in the plate circuit of the tube is approximately proportional to the amplitude of oscillations. Therefore the alternating potentials at the electrodes in the tube can approximately be expressed by kIa, where k is some factor proportional to the resistance of the plate circuit of the tube and also depending on the constant plate potential, if there is such a potential. Since the effect of the alternating potentials on the motion of the electrons must be analogous in its character to the effect of constant potentials, it would seem natural that Barkhausen's formula (2) and our formula (4) should be modified * by replacing Eg by $(Eg \pm nkIa)$ where, according to the P. S. Epstein theory, the sign $+$ has to be taken in the case of normal waves and the sign $-$ in the case of dwarf waves.

The magnitude

$$Ee = kIa \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

represents the effective value of the alternating potentials, and n is a factor depending on the kind of waves. Computations show that a good agreement with experimental data is obtained when the coefficient n is taken to be equal to the ordinal number of the waves, *i. e.*, if we

* This modification may be used in the case of small values of Ia. The reason for this limitation may be seen from § 5 of our article in the Phys. Rev. xli. pp. 226-227 (1932).

take $n = 1$ for normal waves and $n = 2, 3, 4$ for the dwarf waves of the corresponding orders. In this case formula (4) can be written as follows :—

$$\lambda^2(\mathrm{E}g \pm n\mathrm{E}e) = \frac{\mathrm{Const}_0}{n^2} \quad . \quad . \quad . \quad . \quad (8)$$

where the sign + refers to normal waves and the sign — to dwarf waves of all orders. Table II. gives the results of calculations using formula (8) for $k = 6$.

TABLE II.

Normal waves.

Ih (amp.).	Ee (volt).	$\lambda^2(\mathrm{E}g+\mathrm{E}e)$.
0·701	26·4	$6{\cdot}78\times10^5$
0·684	22·5	$6{\cdot}74\times10^5$
0·662	17·4	$6{\cdot}60\times10^5$
0·651	13·5	$6{\cdot}56\times10^5$
0·640	10·5	$6{\cdot}55\times10^5$
0·632	7·8	$6{\cdot}60\times10^5$
0·625	5·4	$6{\cdot}63\times10^5$
0·610	1·8	$6{\cdot}65\times10^5$
	Average	$6{\cdot}64\times10^5$

It is seen from this Table that the value of $\lambda^2(\mathrm{E}g \pm n\mathrm{E}e)$ is sufficiently constant both for normal and for the dwarf waves and, which is still more important, the ratios of the average value of $\lambda^2(\mathrm{E}g + \mathrm{E}e)$ for the normal waves to the average values of $\lambda^2(\mathrm{E}g - n\mathrm{E}e)$ for the dwarf waves is very close to the 2^2, 3^2, and 4^2 which is required by formula (8). The value of Const_0 is calculated from the formula of A. Scheibe.

$$\mathrm{Const}_0 = \frac{2{c_0}^2 dg^2}{2\times10^8}\left[f\left(\sqrt{ln\frac{dg}{df}}\right) - g\left(\sqrt{ln\frac{da}{dg}}\right)\right]^2,$$

where

$$f\left(\sqrt{ln\frac{dg}{df}}\right) = f(x) = xe^{-x^2}\int_0^x e^{u^2}du,$$

$$g\left(\sqrt{ln\frac{da}{dg}}\right) = g(x) = xe^{x}\int_0^x e^{-u^2}du,$$

and df, dg, da are the diameters of the plate, grid, and the filament of the tube respectively, c_0 is the velocity of light, and e/m the ratio of the charge of an electron to its mass. For tubes of the type R 5 (internal diameter of the plate 0·87 cm., diameter of the grid = 0·32 cm., diameter of the filament 0·006 cm.), the value $\text{Const}_0 = 7{\cdot}22 \times 10^5$, which is close to the average value of $\lambda^2(\text{E}g + \text{E}e)$, obtained for the normal waves. This shows incidently, that the normal waves really do correspond to a complete period of oscillations of the electrons about the grid of the tube, or, in other words, to the time it takes the electrons to pass from the filament to the plate and back to the filament, since the formula of A. Scheibe refers exactly to this case. The agreement between the average values of $\lambda^2(\text{E}g - n\text{E}e)$ and the right hand side of eq. (8) shows that the dwarf waves really do correspond to $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$ . . . . of the period of electronic oscillations, as is required by the conditions (5) of excitation of the circuit.

A still better agreement between formula (8) and the observed values could be obtained by selecting k with greater care. This, however, is of no particular importance, since Ia is only an approximate measure of the intensity of oscillations. Therefore, to obtain a better agreement with the observed values, it would be necessary to determine the correction a, of which we have spoken earlier.

It may be mentioned that the calculated effective values of the alternating potentials Ee (Tables II.–V.) are very close to those obtained by direct observations, as it is seen from the preliminary results which were obtained in connexion with an investigation of the problem of the energy of oscillations *.

§ 6. From what has been said above, it is clear that in the case of GM-oscillations the dependence of the wave-length λ on the grid potential Eg must confirm the Barkhausen equation (2) or, in the more general case, our equations (4) and (8) only when the conditions (5) are fulfilled. In other words, when the potential Eg and the natural period T of the circuit connected with the tube change simultaneously.

If we shall change the potential Eg, keeping the period T constant, or conversely, if we shall change the period T,

* G. Potapenko, Phys. Rev. xxxix. p. 551 (1932).

keeping Eg constant, then the conditions (5) will not be fulfilled. The equations (2), (4), (8) also will not be fulfilled. The oscillations will be then possible only

TABLE III.

Dwarf waves, 1st order.

Ih (amp.).	Ee (volt).	λ^2(Eg − 2Ee).
0·701	16·2	$1{\cdot}60\times10^5$
0·684	13·2	1·64 „
0·662	10·8	1·62 „
0·651	7·8	1·67 „
0·640	5·1	1·68 „
0·625	1·8	1·63 „
	Average	$1{\cdot}64\times10^5$

TABLE IV.

Dwarf waves, 2nd order.

Ih (amp.).	Ee (volt).	λ^2(Eg − 3Ee).
0·701	12·0	$0{\cdot}725\times10^5$
0·684	9·6	0·733 „
0·662	4·8	0·755 „
0·651	3·0	0·752 „
0·640	1·2	0·747 „
0·625	0·1	0·733 „
	Average	$0{\cdot}741\times10^5$

TABLE V.

Dwarf waves, 3rd order.

Ih (amp.).	Ee (volt).	λ^2(Eg − 4Ee).
0·701	5·7	$0{\cdot}455\times10^5$
0·684	3·9	0·428 „
0·674	2·1	0·437 „
0·662	0·6	0·431 „
	Average	$0{\cdot}438\times10^5$

in definite rather narrow limits of Eg or T, and their energy will be considerably lower than that of oscillations corresponding to conditions (5). Qualitatively the dependence of the wave-length λ on Eg or on T in these

cases could be accounted for by means of the theory of coupled circuits, as was done, *e. g.*, by F. Tank and E. Schiltknecht and by H. G. Moller *. In order to obtain more exact results, it would be necessary to take into account the dependence of λ on E*e*, which will be variable, and also to take into account the dependence of the natural period T of the circuit on the variation of the internal capacity of the tube. The latter may be done in the manner suggested by K. Kohl †.

§7. Summarizing the results of this paper, it is seen that a fairly exhaustive explanation of the phenomena of the generation of ultra-short waves can be given at the present time. This explanation refers to oscillations of the GM-type, produced using the method of H. Barkhausen and K. Kurz. The explanation covers the case of "normal" waves, the length of which correspond to a complete period of oscillation of the electrons about the grid of the tube, and also the cases of waves of higher orders or "dwarf waves," the length of which corresponds to $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$ . . . . of a period of electronic oscillations.

The lengths of normal and of the dwarf waves can be represented by formula (8) as a function of the dimensions of the tube and of the constant and alternating potentials at the electrodes. This formula is more general than our simpler formula (4), of which Barkhausen's formula (2) is a particular case.

Further investigations are necessary to give an explanation of the phenomena in those cases when the space charges must exercise a great influence on the motion of the electrons (cases $Eg < Es$ and poor vacuum of the tube). Likewise, further investigations are necessary to give an adequate explanation of the phenomena accompanying the generation of oscillations of the BK-type.

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Norman Bridge Laboratory of Physics,
California Institute of Technology,
May 29, 1932.

* H. G. Moller, *Elektr. Nachr. Techn.* vii. pp. 411–419 (1930).

† K. Kohl, *Verh. d. D. Physik Gesellsch.* ix. pp. 36–37 (1928); *Zeits. f. techn. Physik*, ix. pp. 472–475 (1928).

CXVI. *Hyperfine-structure of Arc Lines in Vacuum of Bismuth in the Visible and the Ultra-Violet Regions.* By WALI MOHAMMAD, *M.A.(Punjab)*, *B.A.(Cantab.)*, *Ph.D. (Göttingen)*, *Professor of Physics, and* PREM NATH SHARMA *M.Sc., Research Fellow, Lucknow University**.

PART II.

Term-scheme of Lines.

GOUDSMIT and Back[1], and later on Zeeman, Back, and Goudsmidt[2], have given quite a satisfactory interpretation of the bismuth hyperfine-structure. Back, by his beautiful measurements of Zeeman separations of the hyperfine components, has shown that bismuth nucleus possesses a mechanical as well as a magnetic moment, and that the spin moment of the nucleus is $9/2.h/2\pi$. It has been shown by Aston that bismuth has only one isotope having the atomic weight 209·0, and, therefore, the complicated hyperfine separations in this case cannot be attributed, as in the case of mercury[3] and lead[4] to the different isotopes. An attempt has been made in the following to find the hyperfine separations of the different levels of bismuth[5].

The nomenclature of the levels is that due to Thorsen[6] and modified recently by Pauling and Goudsmit in their book, 'The Structure of Line Spectra' (p. 213).

1. λ 4722·43 $^2D_{3/2}-2s$.

λ in Å.U's.	ν in cm.$^{-1}$	$\Delta\nu$ in cm.$^{-1}$
4722·755	21168·178	
		·180
2·715	68·358	
		·206
2·669	68·564	
		·600
2·535	69·164	
		·228
2·484	69·392	
		·243
2·430	69·635	

$^2D_{3/2}$.

2s.	21169·635	·243	69·392	·228	69·164		
			·828		·806		
			68·564	·206	68·358	·182	68·176

* Communicated by the Authors.

We thus see that the level $^2D_{3/2}$ is four-fold, having separations of ·243, ·217, and ·182 cm.$^{-1}$, while the $2s$ level is double, with a separation of $\Delta\nu = ·817$ cm.$^{-1}$.

2. λ 4121·95 $^2P_{1/2} - 3d''''$.

λ in Å.U's.	ν in cm.$^{-1}$	$\Delta\nu$ in cm.$^{-1}$
4122·271	24251·656	
		1·888
1·950	53·544	
		·717
1·828	54·261	

$^2P_{1/2}$.

$3d''''$.	24254·261		
	·717		
	53·544	**1·888**	51·656

The value of the term-separation of $^2P_{1/2}$ level is 1·888 cm.$^{-1}$.

3. λ 3596·26 $^2P_{1/2} - 4d''$.

λ in Å.U's.	ν in cm.$^{-1}$	$\Delta\nu$ in cm.$^{-1}$
3596·394	27797·727	
		·480
6·332	98·207	
		·556
6·260	98·763	
		·483
6·199	99·246	
		·337
6·088	800·093	

$^2P_{1/2}$.

			7·651
			·556
	27800·093	**1·883**	798·207
$4d''$.	·510		·480
	799·583	**1·856**	7·727
	·337		
	9·246		

The mean value of the term-separation of $^2P_{1/2}$ is 1·870 cm.$^{-1}$, which agrees fairly well with that found for the line

4122, *i. e.*, 1·888 cm.$^{-1}$. Again, the term-separations of $4d''$ are ·556, ·495, and ·337 cm.$^{-1}$.

4. λ 3511·00 $^2D_{5/2}-3d'$.

λ in Å.U's.	ν in cm.$^{-1}$	Δν in cm.$^{-1}$
3511·000	28473·800	
		·552
0·932	74·352	
		·494
0·871	74·846	
		·430
0·818	75·276	
		·349
0·775	75·625	
		·211
0·749	75·836	

No term-scheme can be set up for this line, since there is no ν-difference which repeats itself.

5. λ 3397·310 $^2D_{5/2}-3d'''$.

λ in Å.U's.	ν in cm.$^{-1}$	Δν in cm.$^{-1}$
3397·310	29426·637	
		·563
7·245	27·200	
		·520
7·185	27·720	
		·442
7·134	28·162	
		·295
7·100	28·457	
		·268
7·069	28·725	

Here, too, no ν-difference repeats itself, and hence it is not possible to set up any scheme for this line. However, the ν-differences for this line agree with those of λ 3511. As is shown by Goudsmit and Back, if these ν-differences be divided by 7, 6, 5, 4, and 3 respectively, we get a constant value of approximately ·083 cm.$^{-1}$.

λ 3511.	·552	·494	·430	·349	·211
	·079	**·082**	**·086**	**·087**	**·074**
λ 3397.	·563	·520	·442	·295	·268
	·080	**·087**	**·088**	**·074**	**·089**

6. λ 3076·73 $3d'-{}^2D_{3/2}$.

λ in Å.U's.	ν in cm.$^{-1}$	Δν in cm.$^{-1}$
3076·798	32491·911	
		·159
6·783	92·070	
		·264
6·758	92·334	
		·295
6·730	92·629	

It appears that the ν-differences found in this case are those of the level $^2D_{3/2}$. This becomes still more clear by comparing these separations with the term-separations of the $^2D_{3/2}$-level of the line 4722.

$\Delta\nu\,^2D_{3/2}$ of	**3076**	32492·629	·**295**	92·334	·**264**	92·070	·**159**	91·911
„	**4722**		·**243**		·**217**		·**180**	

The agreement is fairly marked. The $3d'$-level of 3076 does not seem to have been resolved.

7. λ 3067·81 $^4S_{3/2}-2s$.

The satellites of the line 3067 were found to be very diffuse. However, the ν-difference between the components $+0{\cdot}077$ and $0{\cdot}000$ and between $-0{\cdot}085$ and $+0{\cdot}010$ are ·796 cm.$^{-1}$ and ·818 cm.$^{-1}$. Also the separation of the $2s$-level in 4722 is ·824 cm.$^{-1}$. It is probable that the $2s$-level is here reversed. Goudsmit and Back also found a bright reversed doublet of $\Delta\nu \sim 0{\cdot}90$ cm.$^{-1}$.

8. λ 3024·75 $^2D_{5/2}-3d''$.

No term-scheme can be set up since the components could not be resolved.

9. λ 2993·46 $^2D_{3/2}-3d''$.

λ in Å.U's.	ν in cm.$^{-1}$	$\Delta\nu$ in cm.$^{-1}$
2993·502	33395·977	
		·269
3·478	96·246	
		·201
3·460	96·447	
		·167
3·445	96·614	

Here, too, as in the case of 3076, only the $^2D_{3/2}$ level is resolved. The term-separation values in the two cases agree fairly well.

10. λ 2989·15 $^2D_{3/2}-3d'''$.

λ in Å.U's.	ν in cm.$^{-1}$	$\Delta\nu$ in cm.$^{-1}$
2989·191	33444·140	
		·246
9·169	44·386	
		·212
9·150	44·598	
		·157
9·136	44·755	

Here, only the $^2D_{3/2}$-level is resolved, as will be seen by

comparing the term-separation values of this line with those of 4722, 3076, 2993 :

$\Delta\nu\,^2D_{3/2}$ of 4722	·164	·224	·247
„ 3076	·159	·264	·285
„ 2993	·167	·201	·269
„ 2989	·157	·212	·246

11. λ 2938·41 $^2D_{5/2}-4d''$.

This line is a combination of a four-fold term $4d''$ with a seven-fold term $^2D_{5/2}$, and hence the hyperfine-structure is very complicated. That is why there appear only two diffuse and broad unresolved groups of satellites.

12. λ 2898·08 $^2D_{3/2}-3d''''$.

λ in Å.U's.	ν in cm.$^{-1}$	$\Delta\nu$ in cm.$^{-1}$
2898·156	34494·615	
		·202
8·139	94·817	
		·226
8·120	95·043	
		·119
8·110	95·162	
		·143
8·098	95·305	
		·214
8·080	95·519	

$^2D_{3/2}$.

$3d''''$.			34495·519	·214	5·305	·143	5·162
			·702		·690		
	34494·043	·226	94·817	·202	4·615		

Thus the term-separation values of $^2D_{3\,2}$-level are ·226, ·208, and ·143 cm.$^{-1}$, while that of $3d''''$-level is ·696 cm.$^{-1}$. Nagaoka and Mishima get 0·718 cm.$^{-1}$ as the term-separation value of $3d''''$-level. The two values are in fair agreement.

13. λ 2780·53 $^2D_{3/2}-3s$.

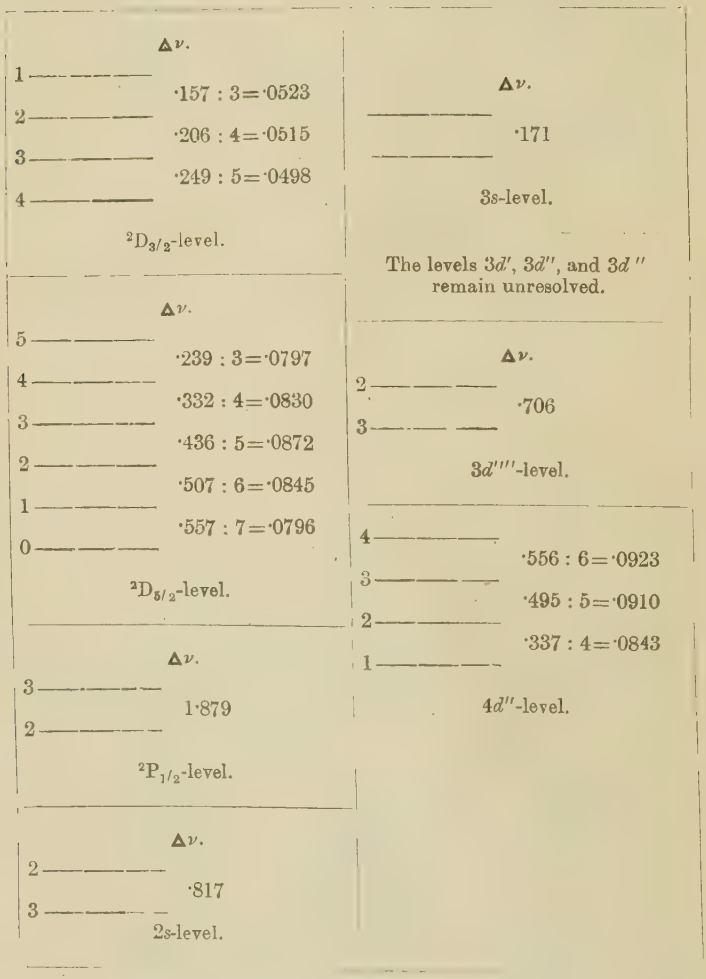
λ in Å.U's.	ν in cm.$^{-1}$	$\Delta\nu$ in cm.$^{-1}$
2780·577	35953·171	
		·151
0·565	53·326	
		·187
0·551	53·507	
		·217
0·530	53.778	

$^2D_{3/2}$.

3*s*.	35953·326	·187	3·507	·271	3·778
	·155		·187		
	3·171	·155	3·326		

TABLE.

The Term-scheme of the various levels of Bi-atom.



In this scheme the component 35953·326 appears twice. The separation of the $3s$-level comes out to be approximately ·171 cm.$^{-1}$.

Conclusion.

The term-schemes of various levels of bismuth have been worked out from the results obtained by the authors in their investigation on the hyperfine-structure of Bi-lines. It is seen that the term-separation values of the different complicated terms of the bismuth atom agree fairly well with those of Goudsmit and Back. In the absence of a suitable source of light, the experiment on Zeeman effect of the hyperfine-structure of this metal could not be carried out. The term-separations of the various terms will be clear from the following table, in which the values given for a particular level are the mean of the different values found for the lines.

The levels $3d'$, $3d''$, and $3d'''$ have not been resolved. It was, however, found by Goudsmit and Back that the levels $3d'$ and $3d'''$ are four-fold and the level $3d''$ is double.

References.

(1) Goudsmit and Back, *Zeit. f. Phys.* xliii. p. 326 (1927).
(2) Zeeman, Goudsmit, and Back, *ibid.* lxvi. p. 1 (1930).
(3) Nagaoka and Mishima, Imp. Acad. Tokyo Proc. ii. p. 248 (1925).
(4) Murakawa, *Zeit. f. Phys.* lxxii. p. 793 (1931).
(5) Wali Mohammad and Sharma, Phil. Mag.
(6) Thorsen, *Zeit. f. Phys.* xi. p. 78 (1923); xii. p. 705 (1924).

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May 1932.

CXVII. *Notices respecting New Books.*

Le Soleil. Par Georges Bruhat. [Pp. 239, 47 figs., 16 plates.] (Libraire Félix Alcan. 20 francs.)

THIS little book gives, in interesting and readable form, the present state of our knowledge of the sun.

The author, as a Professor in the Faculty of Science in the University of Paris, gave a course of lectures on this subject in 1930, and this book represents the substance of his lectures but without the mathematical treatment.

The book is therefore intended as a popular presentation of this interesting subject, and from this point of view fills a useful niche.

There are chapters on the sun's temperature, surface, and rotation; the chromosphere, sun-spots, the corona, and electron emission all receive due attention.

An interesting and readable little volume.

Introduction to Theoretical Seismology. By J. B. Macelwane, S.J., and F. W. Sohon, S.J.—Part II. *Seismometry.* By F. W. Sohon, S.J. [Pp. viii+149.] (New York: John Wiley & Sons. London: Chapman & Hall. 1932. Price 16*s.* 6*d.*)

The writer of a manual of seismometry runs decided risks: he may become too compendious or, on the other hand, too abstract. Father Sohon has taken the risk, and with admirable discrimination produced a volume that is not bulky, but which is coherent and covers the subject in such a way as to be at once a theoretical introduction and a valuable book of reference.

The subject-matter of the chapters is uniformly good. It will suffice to mention that friction is very clearly discussed in Chapter VII. and that the treatment of the Galitzin seismograph is very thorough and practical. The theory of the vertical seismograph is given in sufficient detail to bring out the constructional difficulties that have to be overcome. After reading Fr. Sohon's discussion of irregularities in the paper speed one realizes more strongly than ever that to fit anything other than a high-class driving mechanism to the recording drum is a form of economizing that is little short of ludicrous.

To keep such a work as this within reasonable limits something has of necessity to be sacrificed, and here one rather regrets that the determination of epicentres—after all one of the routine tasks of the seismologist—has received relatively little attention. The space given to vector proofs of the two fundamental theorems on which the method of stereographic projection is based might well have been devoted to such topics as the finding of the best-fitting epicentre when a large number of observations are available. Possibly this matter is discussed in Volume I., but then it would hardly be necessary to refer to Zeissig's method in the present volume.

Another serious defect is the absence of either a bibliography or adequate references. There are many examples that illustrate this. Thus in Chapter X., on the tapping test of a Galitzin seismograph, the treatment follows that of Somville and that of Wilip, but no references are given to enable the reader to follow up the subject in greater detail. Likewise, on p. 131 Fr. Sohon states: "Rudolph and Szirtes have a clever method for the solution of spherical triangles, but the method will not be described because the stereographic method is more convenient." This is needlessly dictatorial: a reference to the work of Rudolph and Szirtes would have enabled an interested reader to judge for himself. On p. 52 it is stated that Seizo Haeno describes a "radio seismograph" in

the 'Japanese Journal of Astronomy and Geophysics.' It is difficult to see why the volume and page are not cited.

Fr. Sohon's sense of humour shows through at times despite the matter-of-fact nature of the subject. He mentions, for instance, that the integration of the equation of forced vibrations "is usually carried out for a simple harmonic earth-motion because the integration is easy to perform and because it is thought that the earth's motion sometimes approximates [to] simple harmonic motion" (the word in brackets is omitted in the book). The aphorism that a sense of humour connotes a sense of proportion is certainly applicable to the volume under review.

Only a few misprints have been noted. The typography is good and the diagrams clear. Some useful tables are given in the text and at the end of the book.

Metallurgy. By Edwin Gregory. With an Introduction by C. H. Desch. [Demy 8vo. Pp. xv+284, with 188 illustrations.] (London and Glasgow: Blackie & Son Ltd. 1932. Price 17*s.* 6*d.*).

This book is described as an introduction to the study of metallurgy, useful primarily to engineers and others interested in this branch of science. It covers a wide field and is divided into two parts. The first part deals with iron and steel and the second part with non-ferrous metals and alloys.

The contents include an account of the manufacture and properties of iron and steel, treated perhaps a little too fully for a book of this size, but, for the engineer the iron-carbon diagram and the heat-treatment of steel are extremely well explained. The chapter dealing with the constitution of metallic systems is, of course, specially important for those interested in the physical and pathological side of the subject, although it is to be regretted that ternary alloy systems should be dismissed in a few lines. It is, however, pleasing to note that peritectic transformations, so frequently ignored in text-books, are adequately described. A great deal of valuable information is given in the chapters on the important subject of "special" and stainless steels. There is also a useful section devoted to the cold-working of metals.

As so frequently occurs in text-books of this kind, there is a relatively small section on the ever-expanding subject of non-ferrous metallurgy. Mr. Gregory's book can be strongly recommended to engineers and also others requiring a lucid explanation of the fundamental principles of the subject as well as much detailed information, useful to the metallurgist.

The book is presented in an interesting manner, and the text and diagrams are well printed.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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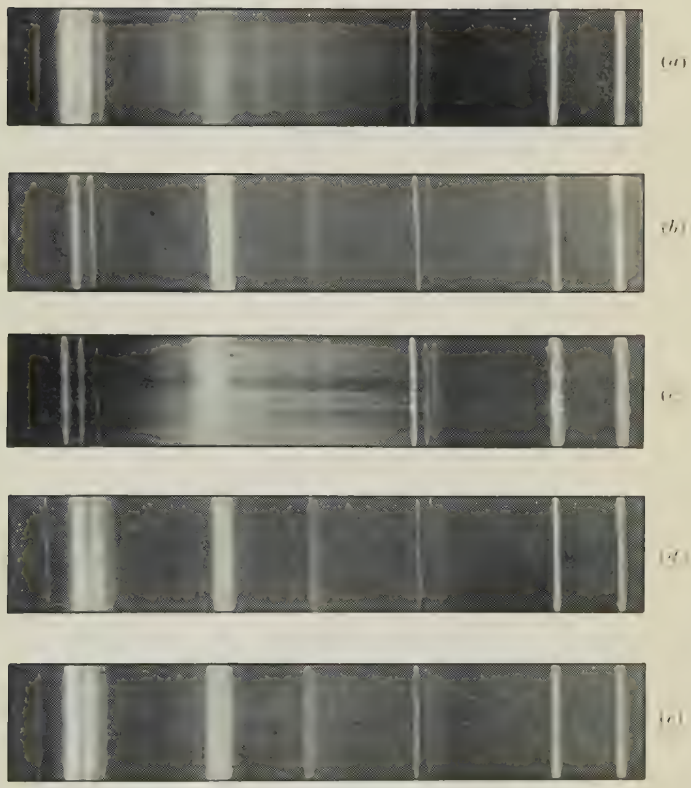
The A- and B-bands of oxygen (A above, B below) photographed at low sun. Thickness of absorbing layer approximately 50 km. The faint lines superimposed on the A band are due to the O_2 O_2 molecule. Both bands are on the same frequency scale.



(*a*) Methyl Nitrate.
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(*c*) Propyl Nitrate.
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